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BALY'S THEORY OF CHEMICAL REACTION AND REACTIVITY.¹

BY WILLIAM M. DEHN.

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This theory, developed since 1904 from voluminous spectrophotometrical studies,² is presented in full in the May number of *THIS JOURNAL*.³ After perusing this and previous contributions one sees that the author has based his theory solely on light phenomena of the ultraviolet region⁴

¹ [Observe Baly's reply following. This criticism of Baly's theory was submitted this summer to Baly by the editor; Baly's reply was also submitted to me by the editor. My additions and counter-replies are all included in brackets, mostly contained in footnotes of this contribution.]

² *J. Chem. Soc.*, 85, 1029 (1904); *Z. physik. Chem.*, 55, 485 (1906); *J. Chem. Soc.*, 87, 766, 1332, 1347, 1355 (1905); 89, 489, 502, 514, 618, 966, 982 (1906); 91, 1122, 1572 (1907); 93, 1747, 1808, 1902, 2108 (1908); 95, 144, 1096 (1909); 97, 571, 1494 (1910); 99, 856 (1911); 101, 1469, 1475 (1912); 103, 91, 2085 (1913); 107, 248 (1915); *Phil. Mag.* [5] 49, 517; [6] 2, 386; [6] 27, 632 (1914); [6] 29, 223 (1915); *Astrophys.*, 42, 4 (1915).

³ *THIS JOURNAL*, 37, 979 (1915); *J. Soc. Chem. Ind.*, 34, 393 (1915). [See also *Astrophys. J.*, 42, 4 (1915), in which Baly claims (in the reply following) to have anticipated and met the objections advanced here.]

⁴ ["It is surprising that in all the work that has appeared dealing with the absorption spectra of organic compounds in relation to their structure, no notice has been taken of the absorption exerted by these compounds in the infra-red region of the spectrum. . . . it has been attempted entirely to decide the constitution from arguments based on ab-

of the spectrum, consequently one hesitates to accept so sweeping¹ a theory, especially when it is remembered that in no case² has the true relation of spectrum-absorption figures to chemical structures or energies³ been demonstrated. Furthermore, when it is remembered that Baly has made purely physical studies⁴ of compounds prepared by his colleagues or by Kahlbaum, and thus he himself has made few original *chemical* observations; or, when it is remembered that Baly presents a theory of chemical dynamics based solely on statical⁵ chemical experiments, one wonders at this invasion of the province of pure chemistry and at this attempted destruction of so many of her sacred temples.

By way of anticipation, it may be stated that, stripped of its novel⁶ and figurative language, Baly's theory of chemical reactivity appears vague and speculative and presents nothing new or useful. Tested by his own data,⁷ it is observed that this theory rests on insufficient experimental evidence⁸ and often on inaccurate observation.⁹

sorption in the ultraviolet and visible regions alone." Baly writes this (*Astrophys. J.*, 42, 5 (1915)), yet he is the greatest offender in this respect, for he has made many spectrometrical studies, all in the ultraviolet region, and has attempted to draw more, varied, and speculative conclusions than any other author.]

¹ See summary. *THIS JOURNAL*, 37, 993. [Observe that Baly's theory renders obsolete LeBel and van't Hoff's theory of stereoisomerism; it relegates to oblivion all chromophoric-group theories of color; "it affords a reasonable explanation of allotropy, magnetic rotation, stereoisomerism, optical rotatory power... the phenomena of isomerism as a whole," of chemical reactivity and reaction, hydrolysis, catalysis and photocatalysis, also of such light phenomena as absorption, fluorescence, phosphorescence. If Baly is not a humorist, he richly deserves the sympathy which he seeks. (*Loc. cit.*)]

² [It will be observed that no such case is attempted to be given in Baly's reply following.]

³ It will be shown below that it is not necessarily true, as Smiles states ("The Relations of Chemical Constitutions and Some Physical Properties," p. 361). "The relations between absorption and constitution must be sought in the dynamic condition of the valencies of the absorbing group."

⁴ [In the reply following, Baly occupies more than half of the space in discussing new physical data not published by him when his theory appeared in *THIS JOURNAL* (see *Astrophys. J.*, 37, 4 (1910)). However this added matter does not appear relevant to the discussion of *chemical reactivity*, though it may throw some new light on the interrelation of absorption, fluorescence and phosphorescence, for a *multiple* relation of these light phenomena may be as independent of chemical reactivity, as the periodicities of sound waves or as the sound waves themselves, are independent of the chemical affinities of the substances which transmit such sound waves.]

⁵ See below.

⁶ Among earlier papers we find such novel phrases as "nascent carbonyl group" (*J. Chem. Soc.*, 89, 491 (1906)), "pseudo-nascent" (*Ibid.*, 89, 492), "chemical reactions in embryo" (*Ibid.*, 101, 1471 (1912)). etc.

⁷ [Much of the data given in this criticism to show the inconsistencies of Baly's theory have been taken from Baly's own papers.]

⁸ [See especially *THIS JOURNAL*, 37, 987-988 (1915); *Astrophys. J.*, 42, 12-16 (1915).]

⁹ [See especially Baly's studies on benzene (*J. Chem. Soc.*, 87, 1332 (1905)). Com-

Though modifying his views, theories¹ and methods² as new conditions arose during the past decade, Baly has clung tenaciously to one phrase, "the open and closed force-fields." This he offers as *the* explanation of chemical reactivity and most other chemical phenomena.

However, it may be stated at once, if the old terms *chemism*, *chemical affinity*, *chemical potential*, or *chemical intensity* be re-substituted³ throughout for "force-fields," whose true nature, of course, remains unknown, it is observed that no new light is thrown on chemical reactivity. With this and with other terms, one cannot escape the impression that Baly is clothing familiar concepts in new language and it scarcely needs to be

pare with Hartley (*Proc. Roy. Soc.*, 80, 162 (1907)) or see also Kayser's "Handbuch der Spectroscopie," Vol. III, pp. 483-5.]

¹ It is interesting to find in Baly's later papers no reference to the word *isorropesis*, coined by him (*J. Chem. Soc.*, 89, 498 (1906)) and used in a series of papers to designate "potential tautomerism." In the words of Baly and Desch (*Ibid.*, 87, 768 (1905)): "No organic substance shows an absorption band unless a possibility of tautomerism exists in the molecule." The dynamic changes of such tautomeric parts of molecules were described by the word "isorropesis;" that is, isorropesis is the cause of absorption bands. In Shephard's recent text-book on "Photochemistry," p. 189, we read: "Baly's theory of isorropesis. . . . at once begs and solves the problem."

[It would be interesting to know if Baly still believes in his isorropesis theory. It and his present theory to account for absorption phenomena are different, if not contradictory; hence, at least for the purpose of clarification of the literature (see especially the Ramsay series of text-books on physical chemistry), it would be fair to withdraw this earlier theory, if it is no longer tenable. So also in respect to the theory of vibration of the benzene ring, a theory based on coincidental relations of carbon linkings in the molecule and absorption bands in a limited portion of the spectrum (Baly and Collie, *J. Chem. Soc.*, 87, 1332 (1905); 89, 514 (1906)). See also Hartley (*Ibid.*, 87, 1826 (1905)). If this theory also is untenable, why not withdraw it? If the earlier theories were incorrect, what salvage can be expected to be made from the present speculations?]

² Until recently the iron arc was used by Baly as the source of light in his spectrophotometrical studies. Now he uses arcs containing salts of cadmium, uranium, and molybdenum. (Compare *J. Chem. Soc.*, 85, 1029 (1904) and 99, 856 (1911).) [If the earlier experiments involved errors resulting from imperfect illumination, what confidence can we place in conclusions drawn from these earlier experiments? Baly's chief support for his theories is based on experiments involving use of the iron arc (*J. Chem. Soc.*, 93, 2108 (1908); 101, 1475 (1912); *THIS JOURNAL*, 37, 987-88; *Astrophys. J.*, 42, 12-16). Why not reinvestigate with the modern arc? What assurance have we that the present methods also do not contain errors? If spectrometrical methods are not at present absolutely reliable (like the use of balance) how can such spectrometrical studies be made the experimental basis of a theory that comprehends and explains all chemical phenomena?]

³ [Does Baly intend that the energies, chemical affinity and opened-up force-fields are the same and may be taken synonymously? If conceived to be different, does Baly consider himself to have discovered a new force of nature? Does Baly conceive of the successive opened-up stages of force-fields to be portions of the total chemical affinity?]

remarked that the paraphrasing of a concept no more adds new information than does transliteration or translation of the same.

Let us note some other definitions of Baly. *Residual affinity*¹ is defined as "the uncompensated balance of force-lines," or "uncompensated residuum when the maximum possible condensation of force-lines of the molecule has taken place."

*Valency*² is defined as a "resultant effect of force-lines," or "inter-atomic rearrangement of electrons when the potential gradients within the additive complexes first formed are sufficiently steep," or "transference³ of one or more electrons along the potential gradients which is set up by the condensing together of the force-fields arising from the electromagnetic fields of two atoms of opposite type."

A *chemical reaction*⁴ "between molecules depends on these force-fields . . . and will occur only when the gradient within the complex first formed is sufficiently steep to cause the electrons to migrate."

It appears⁵ that "shallow and steep potential gradients" are only less and greater chemical reactivities. It would seem also that Baly's own force-fields have "been invoked to play the rôle of *deus ex machina*⁶ and relieve the exigencies of the situation."

When we inquire further what Baly's conception of force-fields is, we find⁷ "each atom . . . is the center of a field of force, the lines of which radiate in every direction." Elsewhere we read⁸ that these force-fields "have been proven to exist in the immediate neighborhood of the atoms." Compounds also are supposed to have force-fields which are so complex that they present a veritable "net-work⁹ of potential gradients."

Now though it may be possible to demonstrate the existence of "force-fields" such as Baly describes, certainly his experiments have not demonstrated them, indeed, his experiments have not necessarily indicated

¹ [THIS JOURNAL, 37, 982 (1915); *J. Chem. Soc.*, 101, 1469 (1912). Observe the last paragraph of Baly's reply following: "Every chemist of the present must surely recognize the possession by compounds, saturated as regards their primary valencies, of properties which may best be classified as residual affinity." I beg of him to present some one *chemical* property of hexane, of any paraffin hydrocarbon, or, indeed, of any *saturated* compound, that can or must be referred to residual affinity such as he describes.]

² THIS JOURNAL, 37, 983 (1915); *J. Chem. Soc.*, 87, 784 (1905); *Astrophys. J.*, 23, 110. Baly's earlier conception of valency seems to have been elastic tube-like structures.

³ THIS JOURNAL, 37, 980 (1915).

⁴ *Ibid.*, 37, 981 (1915).

⁵ *Ibid.*, 37, 983-4 (1915).

⁶ *Ibid.*, 37, 982 (1915).

⁷ *J. Chem. Soc.*, 101, 1469 (1912).

⁸ THIS JOURNAL, 37, 982 (1915). Perhaps no one denies that all atoms possess energies or forces usually called chemical affinity.

⁹ THIS JOURNAL, 37, 986 (1915).

the probability of such "force-fields." This will become evident when examination is made, especially of the mode of "opening and closing" of such "force-fields."

That it may be shown at once that the *modus operandi* of "force-fields" is vaguely conceived and Baly's whole theory rests on insufficient observation and experiment, a quotation¹ from his summary is made. "To the closed force-fields and their opening-up by the influence of solvents or light may be attributed all phenomena of chemical reaction." Evidently Baly conceives of *light* or *solvents* or both as the only causes of such "opening of closed force-fields" (chemical reactivity). Apparently he overlooks heat,² pressure, electricity and other dynamic causes of chemical reaction. This oversight is remarkable since to the chemist, *heat*, in the presence or the absence of solvents, is far more important than light³ in promoting chemical reactions. By way of an example it needs here only to be recalled that nearly all organic substances are decomposed at high temperatures, consequently "force-fields" must be opened by heat also.

It must not be denied that the validity of his theory possibly may be established on the basis of study of solvents and light only. However, a theory which is claimed to be a fundamental explanation of "all the phenomena of chemical reaction" certainly must include all "openers" of chemical reactivity.

Now, Baly conceives⁴ of these force-fields to be "more or less closed"

¹ THIS JOURNAL, 37, 993, also p. 984 (1915).

² Perhaps the observation (*J. Chem. Soc.*, 101, 1475 (1912)) that "the vapors of ammonium chloride and mercurous chloride... possess force-fields so condensed that increase of temperature alone is not sufficient to open them," has led Baly to believe that all force-fields are resistant to opening by heat.

³ It is not clear whether Baly believes that chemical reactions may take place in the dark. Certainly it follows as a corollary from the quotation above that substances not in solution would not react in the dark. Some discussion of reactions in the absence of light is given by Baly. (See *J. Chem. Soc.*, 87, 1333 (1905).) [See Baly's most recent paper (*Astrophys. J.*, 42, 8 (1915)), wherein he again states that the unlocking of chemical affinity "may be brought about in one of two ways: namely, by the use of a substance possessing residual affinity or by the action of light." See now Baly's reply following, wherein he acknowledges *other* dynamic causes of chemical reaction. Note here also, by the way, the following: "Every molecule considered in a free state has a minimum reactivity... it must absorb... energy before it can react... at least one quantum of energy." "However, there are known to chemists so many experiments wherein chemical reactions take place spontaneously, without the application of energy, without the medium of a solvent and, indeed, *give off energy*, that this new conception of Baly is surprising, to say the least."]

⁴ THIS JOURNAL, 37, 982 (1915). See Mellor's "Statics and Dynamics," Chap. VI, for a discussion and bibliography on the "period of induction." Evidently what Baly calls "closed force-fields" has been known since the beginning of the nineteenth century. [Perhaps the best characterization of Baly's theory is that he has rediscovered chemical affinity.]

but, being opened, "the previously closed fields become endowed¹ with reactivity." Moreover, "the opening-up of a complex field must take place in definite stages² . . . called into play by the use of suitable solvents" and "if the opening-up process is carried to the farthest possible extent . . . ionic dissociation³ is the sequence."

The state of affairs thus indicated would necessitate *ex hypothesi* different affinity constants for the same substance as the successive stages were opened up and yet other affinity constants for the same substance in different solvents,⁴ propositions impossible to demonstrate and conditions difficult to conceive of, especially when solutes are contained in non-ionizing media. Furthermore, since changes of concentration, pressure and temperature⁵ have marked effects on absorption bands, various other stages,⁶ indeed, an infinite series of stages, must be assumed. Now Baly would have us believe "each stage is characterized by its light absorptive power⁷ . . . and each stage possesses a definite reactivity," therefore, we must assume not only an infinite series⁸ of absorption curves but an infinite series of reactivities and consequent reactions and products. These results, of course, are contrary to fact,⁹ contrary to the chemist's conceptions of valency, and contrary to the fundamental laws of definite, multiple, and equivalent proportions.

[There can be no quibble that Baly believes that molecules plus energy coincidentally and inevitably cause: (1) "opened-up stages," (2) chemical reactivities and (3) "definite vibration"¹⁰ frequencies." Now if chemical reactivities and spectral phenomena are co-existent properties, all molecules showing definite vibration frequencies must show chemical reactivities and all chemically reactive molecules must show definite vibration frequencies. That the former of these is not necessarily true is proven by the inert gases helium, argon, etc., which show definite vibration frequencies but no chemical reactivities. On the other hand, that

¹ THIS JOURNAL, 37, 984 (1915).

² *Ibid.*, 37, 986 (1915). See also *J. Chem. Soc.*, 103, 2086 (1913). "We have now succeeded . . . in recognizing several distinct stages."

³ THIS JOURNAL, 37, 985 (1915).

⁴ See the various absorption curves of acetoacetic ester and ethoxycrotonic ester in different solvents (*Hantzsch. Ber.*, 43, 3058-9 (1910); Baly, *J. Chem. Soc.*, 85, 1034-9 (1904)).

⁵ Kayser's "Handbuch der Spectroscopie, Vol. III, pp. 128-141; see also studies by Purvis. In the reply following, observe how Baly treats this objection.

⁶ Baly and Krulla, *J. Chem. Soc.*, 101, 1472-3 (1912).

⁷ THIS JOURNAL, 37, 987 (1915).

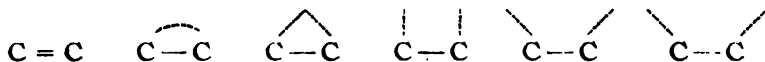
⁸ See for instance some of Baly's curves (*J. Chem. Soc.*, 85, 1039). Varied quantities of hydrogen chloride will give curves covering the entire area between the upper and the lower curves, hence an infinite number of curves.

⁹ [As acknowledged by Baly in his reply following.]

¹⁰ [See THIS JOURNAL, 37, 993 (1915); also Baly's reply following.]

all chemically reactive molecules cause definite vibration frequencies is not only undemonstrable but improbable. This improbability is shown: (1) by the fact that certain molecules react in the dark without developing light phenomena and (2) by the *non-proportionality* of chemical reactivity and vibration phenomena: (a) certain solids and colored substances may show considerable spectral activity but little or no chemical reactivity, (b) the most chemically reactive substances are not necessarily the most active spectrally. In this connection it may be stated that, since Baly now acknowledges *heat* to be an "opener of chemical reactivity," it may be easier for him to understand that light frequencies may possibly be independent of chemical reactivity.]

At this time it must be observed that Baly has never indicated by figures what his conceptions are of "stages" of "opened-up force-fields." Since these have been left to our imagination, some visualization of them is not only permissible but necessary. Therefore, we depict them as follows:



wherein each indicated stage and their intermediate forms are assumed (with Baly) to possess specific chemical and light-influencing properties. Though such an explanation is conceivably simple¹ and elastic, it must be remembered that these stages are purely speculative, are contrary to the conventional conceptions of structural chemistry, and, until some proof of their existence² is advanced, can serve no useful purpose.

Let us now examine more in detail the "mechanism of the opening of a closed force-field." "If the molecules of a compound,³ the force-fields of which are closed, be brought into the neighborhood of the molecules of another compound possessing residual affinity, the force-lines of the latter will interpenetrate the closed fields of the former, with the result that they will be opened and endowed with enhanced reactivity. . . . the case is an absolutely general one."

¹ Apropos of its claimed simplicity, the following quotation is made: "One advantage of the theory may perhaps be touched upon, namely, it does away with the somewhat alarming complexity which Hantzsch's doctrine of one adsorption curve one structure introduces into organic chemistry." (*J. Soc. Chem. Ind.*, 34, 399 (1915)). However, note Baly's "veritable net-work of potential gradients" in molecules. (*THIS JOURNAL*, 37, 986 (1915).) If imperfect correlation of absorption curves and chemical structures are impossible, thereby (according to Baly) invalidating the quinonoid theories of color, why does not this same imperfect correlation of absorption curves and "opened-up stages" cast discredence on Baly's theory? It must furthermore be remembered that absorption phenomena possibly are independent of specific structures and chemically active groups.

² See Baly's reply following, in which he acknowledges his lack of proof: "I make no attempt to demonstrate the existence of the force-fields."

³ *THIS JOURNAL*, 37, 396 (1915).

Here and elsewhere in Baly's papers we are led to believe that the residual affinities of the solvent open up the force-lines of the solute. But, by way of an example, let us consider *hexane, a saturated compound not possessing residual affinity*. Judged by its light-absorption curves,¹ solutes are affected by hexane in the same manner as by other solvents which are held to possess residual affinity. Hence it cannot be maintained by Baly that in all cases the force-lines of the solvent open up, interpenetrate, and endow solutes "with enhanced reactivity," neither can it be maintained that such changes in absorption spectra as result from dissolving substances in hexane are brought about by the residual affinities or "force-lines of the solvent."

Further, Baly dogmatically states² "that addition complexes between solute and solvent, usually known as solvates . . . always exist when such molecular types are brought together." However, it must be remembered that with paraffin hydrocarbon solvents this is impossible, since these compounds are saturated,³ possess no residual affinities and have not yielded such molecular compounds.

Nevertheless, let us see what two experiments Baly⁴ gives to "prove the existence of . . . intermediate stages" which he claims "afford proof of the force-field theory."

The aminobenzaldehydes are⁵ nearly colorless or yellow substances giving one absorption band in alcoholic solution; with a little hydrogen chloride their alcoholic solutions, but not their aqueous solutions, are more deeply colored and give two absorption bands; with an excess of hydrogen chloride, their alcoholic solutions become colorless and show one band. All three absorption curves are different.⁶ Now to account for the second absorption band and the increase of color, Baly⁷ assumes an "*intermediate form which reacts with more acid to give the salt*." In other words, here and elsewhere Baly makes the following chain of assumptions:

¹ Hantzsch, *Ber.*, 43, 3058-74 (1910); see also Baly's curves for picric acid (*J. Chem. Soc.*, 103, 2094 (1913)) which was dissolved in *heptane* and other solvents such as (a) alcoholic HCl and (b) dimethyl aniline. Observe that all these curves do not differ widely, though heptane is devoid of residual affinity and the other solvents are not.

² *THIS JOURNAL*, 37, 984 (1915); *J. Soc. Chem. Ind.*, 34, 396 (1915).

³ That residual affinities are not necessarily correlated with absorption bands must be concluded from studies of the absorption spectra of paraffin hydrocarbons. See Kayser's "Handbuch der Spectroscopie," Vol. III; methane, p. 529; ethane, p. 263; butane, p. 369; hexane, p. 517; heptane, p. 216; octane, p. 540. It is observed that, while showing absorptive spectra, these compounds are devoid of residual affinity.

⁴ *THIS JOURNAL*, 37, 987-8 (1913); *J. Chem. Soc.*, 93, 2110 (1908); 101, 1475 (1912); *Astrophys. J.*, 42, 11-15 (1915). The data of these two studies constitute the basis of Baly's theory.

⁵ *THIS JOURNAL*, 37, 987; *J. Chem. Soc.*, 93, 2108 (1908).

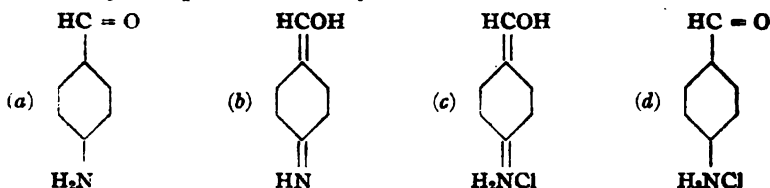
⁶ *Loc. cit.*

⁷ *THIS JOURNAL*, 37, 987 (1915).

color \rightleftharpoons absorption bands \rightleftharpoons intermediate compounds \rightleftharpoons
 opened-up stages \rightleftharpoons force-fields \rightleftharpoons theory of chemical reactivity.

[Baly recognizes here the probable formation of a compound intermediate to *p*-aminobenzaldehyde and its hydrochloride. Even if the existence of this assumed intermediate compound were proved by chemical methods of separation, its existence *per se* would not prove the existence of an "opened-up stage" such as Baly assumes. By way of an example, if ammonia is treated with an excess of an alkyl iodide, quaternary alkyl ammonium iodide is formed as the end product and *six definite intermediate compounds* (the respective primary, secondary, tertiary bases and their salts) are formed. Here no assumptions of opened-up stages such as Baly conceives of are recognizable or are necessary to account for all the phenomena.]

Let us consider how, on the other hand, the above facts can be accounted for by the quinonoid theory:



Here, of course, two intermediate products are assumed; this¹ quinonoid explanation, therefore, may not be correct; but Baly's explanation also may not be correct, for he also makes two assumptions,² and, while so doing, offers the above example as "a definite *proof* of the force-field theory."

Now let us examine Baly's second example³ which⁴ "establishes beyond any doubt the existence of the intermediate stage in a chemical reaction such as was deduced from the force-field theory."

Absorption spectra were taken of *p*-nitroaniline (1) in alcohol, (2) in sulfuric acid and (3) in sulfuric acid after warming. Different curves were obtained in the three cases. Baly states, "we have evidence that the whole of the *p*-nitroaniline is converted into the intermediate phase." This evidence of total conversion or, indeed, of partial conversion is not

¹ Observe how (a) and (b) account for the original colorless and colored forms of the compounds. Also observe how Baly's theory fails to account for the original colors. Finally observe Baly's anomalous reaction of the addition of hydrogen chloride to the hydrochloride of the original *p*-aminobenzaldehyde (see *Astrophys. J.*, 42, 12 (1915)).

² These assumptions are: (1) modified absorption figures indicate changes of composition; (2) these changes of absorption and composition indicate molecular addition.

³ *J. Chem. Soc.*, 101, 1475 (1912).

⁴ *THIS JOURNAL*, 37, 988 (1915).

given in the paper.¹ Now, while not denying that he possesses such evidence, or that an intermediate compound can be formed in this case, it must be remembered that Baly is assuming here that every change of absorption curve indicates a change of chemical composition. That this is true has not been demonstrated; on the contrary, that this is not true, has been indicated by various absorption studies.²

Now since the existence of intermediate compounds, in the two cases given, is merely *assumed*, no real proof of Baly's theory is submitted. Furthermore, even though the alleged intermediate compounds could be proven, they would not in themselves, nor would their absorption curves, constitute evidence of "opened-up force-fields," for myriads of intermediate molecular compounds are recognized by chemists without postulating or necessitating a condition of "stages" or "opened-up force-fields."

Let us next consider how *light*, as well as solvents, "open up closed force-fields." Let us see,³ indeed, "how the whole of the phenomena of photocatalysis can be explained." This explanation follows. "Due as they are in the first place to the rotation of the electrons of the constituent atoms, it follows that the force-fields must be capable of absorbing these rays of light which have the same frequency⁴ as that of the electrons. The light in being absorbed does work upon the closed field and opens them, and this gives a rational explanation of the selective absorption of light."

It is observed that this "rational" explanation involves the following assumptions: (1) the electronic composition of all matter, (2) rotation of electrons, (3) synchronous vibrations of electrons and rays of light, (4) transference of some light energy into chemical energy, and (5) consequent maintenance of force-fields in an "opened-up state." It would seem that much light is necessary for all this.

Now while remembering⁵ "the primary assumption that there exists a definite correlation between the constitution of a compound and the power which it exerts of absorbing light" or, in other words, while believing with Baly that each absorption line, band, or general absorption area is caused by a different and definite "opened-up stage," let us see what conclusions can be drawn from absorption spectra of pure substances.

¹ *Loc. cit.*

² See the various absorption curves of acetoacetic ester, etc., in different solvents: Hantzsch, *Ber.*, 43, 3057-74; Baly and Desch, *J. Chem. Soc.*, 85, 1034-39; see also Purvis' papers for more rational explanations of absorption bands.

³ *THIS JOURNAL*, 37, 986 (1915).

⁴ It is possible that rays of light whose frequencies *differ* from the frequencies of the electrons are the ones that are absorbed. That photochemical substances, so simple as silver halides are sensitive to a wide range of light rays suggests such a possibility.

⁵ *J. Soc. Chem. Ind.*, 34, 394 (1915); *THIS JOURNAL*, 37, 979 (1915).

Consider first the simple substance water. We find¹ that it gives a multitude of absorption lines and bands, hence we must conclude with Baly that it possesses a multitude of "opened-up stages" and a multitude of different reactivities.

Or let us consider benzene. Hartley and Huntington² found in the ultraviolet spectrum seven absorption bands; this was confirmed by Baly and Collie.³ The latter authors demonstrate geometrically that benzene can have only seven "stages," hence a striking "agreement between facts and the theory" is claimed. Now since this illustration is often quoted and is used as the basis of a dynamic theory⁴ of the benzene system, it must be recalled not only that liquid benzene itself exhibits numerous bands in the visible and the infra-red regions of the spectrum,⁵ but Hartley⁶ has shown, when in the form of vapor, benzene gives *eighty-two bands*. It is evident that this theory, based on coincidental relations of absorption bands in a portion of the spectrum, to pulsating linkings or "opened-up stages," must fall.

Notice further what erroneous conclusions may be drawn from a limited portion of the spectrum. On the one hand, we find benzene giving more than seven bands, while, on the other hand, we find naphthalene⁷ giving only *three* bands. According to Baly's theory, the latter possessing more structural linkings,⁸ should have more bands and more "stages," but such is not the case, hence again the theory is shown to be inconsistent.

¹ Kayser's "Handbuch der Spectroscopic," Vol. III, pp. 389-399. See Baly's vague discussion of hydration, *THIS JOURNAL*, 37, 983 (1915).

² *Phil. Trans.*, 170, 257 (1879). Hartley and Dobbie found only six bands, *J. Chem. Soc.*, 73, 695 (1898).

³ *J. Chem. Soc.*, 87, 1335-6 (1905). Grebe gives eight bands, *Z. wiss. Phot.*, 3, 376.

⁴ *J. Chem. Soc.*, 71, 1013 (1897); 87, 1826 (1905); 89, 514 (1906). Also see Smiles's text-book (p. 383) and other text-books of the Ramsay series.

⁵ Kayser's "Handbuch der Spectroscopic," Vol. III, pp. 483-5.

⁶ *Proc. Roy. Soc.*, 80, 162; *Phil. Trans.*, 208, 475 (1908). [In the reply following, Baly quibbles over the use of the term *absorption band*. In this paper I have always quoted and used this term in the sense and words of no less authority than Kayser (and Baly himself). As the result of recent studies, however, Baly would now have us believe "by the term absorption band is always meant an absorption band group." Notice, a *band* is a *band group*. Until these become interchangeably and commonly accepted I must beg to limit my use of these terms to the common usage of the literature. It would be interesting to have Baly state how many absorption bands, absorption band groups and absorption lines the simple compound benzene gives. (See Baly, *Astrophys. J.*, 42, 32-35 (1915).) Also how many "molecular phases" or "opened-up stages" does benzene possess?]

⁷ Baly and Tuck, *J. Chem. Soc.*, 93, 1902 (1908); Stokes and Soret, *Arch. soc. phys. et nat.*, [3] 9, 513; Hartley, *J. Chem. Soc.*, 47, 685 (1885).

⁸ Baly and Tuck, *J. Chem. Soc.*, 93, 1905 (1908). "Naphthalene... consists of two rings of which one is truly benzonoid." See here also Baly's effort to bolster up his isorropesis theory.

Though no good reason has ever been given why all the spectral bands¹ should not be used in studies on the relation of absorption spectra to chemical constitution and chemical dynamics, Baly and others have made use almost exclusively of the ultraviolet region. Recently² Baly realizes the importance of infra-red bands for we read: "It would seem obvious that there must be an intimate connection between all the absorption bands exerted by a compound, in whatever region of the spectrum they may occur."

Therefore, while making use of all available absorption lines and bands, let us examine simple and closely-related substances to see if they correlate with dynamic groups, linkings, or "opened-up stages." The following³ may be taken as typical examples: nitric acid-8; chloroform-15; methyl alcohol-13; ethyl alcohol-13; ethyl bromide-27; ethyl nitrate-10; acetic acid-9; paraldehyde-15; amyl alcohol-19; valeric acid-10; toluene-35; aniline-36; nitrobenzene-11; mesitylene-34; turpentine-13; thymol-22; brombenzene-10; picoline-24; pyridine-23, etc.

Correlations of these lines, bands and non-enumerated general absorption areas, with definite structures or "opened-up stages" of the respective molecules are evidently impossible. But the problem is further complicated by a large increase of lines and bands when the substances are studied in the form of vapor.

Hartley,⁴ Purvis⁵ and others have recently shown that many compounds, studied spectrophotometrically in the form of vapor, give larger general absorption areas, and stronger, wider and more numerous bands, than at ordinary temperatures. Furthermore, varied pressures give similar effects. For instance, with piperidine Coblentz⁶ finds one band in the infra-red; Hartley⁷ and Purvis⁸ find no band when it is viewed in an alcohol solution; however, in the form of vapor at 332 mm., Purvis⁹ finds *fifteen bands*.

Other results obtained by Purvis, working with compounds at varied temperatures and pressures, are as follows: pyridine¹⁰ (14° and 758 mm.),

¹ Kayser's "Handbuch der Spectroscopie," Vol. III. See here complex spectra of simple substances. See also Purvis' series of papers, *Proc. Camb. Phil. Soc.*, 14, 381, 436, 568 (1907); *J. Chem. Soc.*, 95, 294; 97, 692, 1035, 1546, 1648; 99, 2318.

² *J. Chem. Soc. Ind.*, 34, 394 (1915); *Astrophys. J.*, 42, 4 (1915).

³ These figures are taken from Kayser's "Handbuch der Spectroscopie," Vol. III. Owing to conflict of authorities, the numbers given cannot be vouched for. However, they are probably more numerous than indicated.

⁴ *Phil. Trans.*, 208, 475.

⁵ See references above.

⁶ *Astrophys. J.*, 20, 207.

⁷ *J. Chem. Soc.*, 47, 685.

⁸ *Ibid.*, 97, 712.

⁹ *Ibid.*, 97, 710.

¹⁰ *Ibid.*, 97, 694.

38 bands; α -picoline¹ (15° and 745 mm.), 14 bands; nicotine² and coniine, no bands; quinoline³ (60° and 865 mm.), one band; aniline⁴ (14° and 763 mm.), 83 bands; homologs of aniline, in the form of vapor, no bands; furane⁵ (13° and 749 mm.), 15 bands; furfural⁶ (12° and 158 mm.), 21 bands; pyrrol⁷ (17° and 760 mm.), 4 bands.

From these and other studies the conclusion is drawn that *absorption bands cannot at present be correlated⁸ with chemical structures, linkings, dynamic groups, or "opened-up stages."* On the contrary, as was pointed out by Purvis,⁹ "a complete explanation of the origin of selective absorption implies a consideration of many and deep-seated factors." Such explanation¹⁰ implies "a balance of a complex series of disturbances, and the forces which determine these include such factors as the number, the mass, the intrinsic characters, and the orientation of the atoms of both the nucleus and the side-chains; the physical conditions of the vibrating system as vapors or in solution or as liquids at various temperatures and pressures: and on the disturbances and reaction of the vibrations consequent on the absorption of the radiant energy by the various oscillating atoms and atomic groups."

Another observation on absorption studies must be made. The ordinary absorption curves, plotted, as they are, from the limits of positions of absorption bands, that is, each band at each observed thickness supplying two points on the coördinate field and all points being linearly connected, must be regarded as *position* curves and cannot properly be interpreted as *dynamic* curves. However, such dynamic interpretations are frequently and erroneously implied or made, yet such interpretations probably are as fallacious as an *object-associated, dynamic* interpretation of a curve derived in a similar manner from the limits of shadows of such object illuminated by an approaching light.

In this connection it must be recalled that the primary assumption in

¹ *J. Chem. Soc.*, 97, 700.

² *Ibid.*, 97, 1036. Nicotine shows one band in alcohol solution.

³ *Ibid.*, 97, 1038; 47, 685. Shows three bands in alcohol solution.

⁴ *Ibid.*, 97, 1548.

⁵ *Ibid.*, 97, 1648.

⁶ *Ibid.*, 97, 1650.

⁷ *Ibid.*, 97, 1655.

⁸ [In his most recent paper (*Astrophys. J.*, 42, 4 (1915)) and in the reply following, Baly attempts to correlate absorption groups, bands, and lines of the entire spectrum. How well he has done this remains to be seen. However, it must be remembered, as stated above, such correlations may be irrelevant to the phenomena of chemical reactivity. After persuing all of Baly's recent papers, the conviction remains, whereas he has multiplied words and made many dogmatic statements in respect to chemical reactivity, he has thrown no new light on chemical activity and has not, in any one instance, correlated light-vibration phenomena with a definite chemical reactivity.]

⁹ *J. Chem. Soc.*, 97, 1659 (1910).

¹⁰ *Ibid.*, 99, 2325 (1911).

correlations of absorption phenomena and chemical constitution, is that similarity of curves indicates similarity of dynamic groups. That this is not true is evident not only in all cases of curves whose ordinates are thicknesses of the same solution¹ but also in studies of the curves themselves.

If comparisons are made of the curves of certain divergently constituted compounds as, for instance, aniline² and tetrachloropyridine³ and acetylacetone⁴ and ethyl cinnamate,⁵ *p*-aminobenzaldehyde hydrochloride⁶ and 4-nitro-*o*-xylene⁷ and *p*-nitroanisole,⁸ *p*-aminobenzaldehyde⁹ and nitrofluorene,¹⁰ etc., it will be observed that their curves are respectively not only nearly identical but that they differ far less widely than the curves of homologs¹¹ or of the same substance in different solvents. Surely, in the light of our present knowledge, it is hopeless to attempt to correlate absorption phenomena and dynamic groups of so divergent compounds.

Another important observation on absorption spectra studies must be made at this time. Hartley's early experiments were based on studies of different concentrations in equal thickness. Later the method, almost universally employed by Hartley, Baly and others, involved different thicknesses of the same solution. This latter method, while more convenient, brings into the viewed field *static molecules*, hence involves no chemical change other than chemical equilibria. The former method, involving equal thickness of varied concentrations, brings into the viewed field molecules whose number is progressively modified by the solvent,¹² the chemical changes thus resulting being, of course, such as are produced by ionization, hydrolysis, etc. This latter method, therefore, must be more fitted for study of the "opening-up" influence of solvents

¹ See below.

² *J. Chem. Soc.*, 87, 1343.

³ *Ibid.*, 91, 1124.

⁴ *Ibid.*, 85, 1034.

⁵ *Ibid.*, 93, 1812.

⁶ *Ibid.*, 93, 2110.

⁷ *Ibid.*, 97, 574.

⁸ *Ibid.*, 89, 518.

⁹ *Ibid.*, 93, 2110.

¹⁰ *Ibid.*, 97, 577.

¹¹ *Ibid.*, 87, 1342-3 (1905); 93, 2110 (1908). Compare benzene and ethyl benzene; aniline, methylaniline and dimethylaniline; *o*-aminobenzaldehyde and *p*-aminobenzaldehyde.

¹² Recently Baly realizes the important influence of concentration on absorption (*J. Chem. Soc.*, 101, 1471 (1912)). "Variation of dilution in any one solvent at once gives an explanation why Beer's law fails to hold in so many cases." Later (*Ibid.*, 103, 91 (1913)), Baly studied acetoacetic ester and pyridine through such a range of concentrations as 10 *N* to 0.0002 *N*, and observed that the "step-out," or limits of transmission of bands, varies progressively but not in accordance with Beer's law.

than the former. Now, since Baly's theory is built up primarily on such "opening-up by solvents," it seems remarkable that his experiments are based on the very method which cannot readily show "opening-up by solvents."

It may be maintained that, by changing the concentration of solutions and viewing these in equal thicknesses, spectra are obtained which show the progressive influence ("opening-up") of the solvent. However, attention must be called to the possibility that, even when the solute is not modified by the solvent, such solute molecules themselves may influence the rays of light in some manner similar to finite *masses*; that is, a *grouping* or *clumping* of solute molecules in concentrated solutions and a *thinning-out* by dilution may be factors in absorption phenomena.

Summary.

1. Baly's theory, "the force-field theory," is given as an explanation of chemical reactivity and other chemical phenomena.
2. This theory is based entirely on light-absorption phenomena, the true nature of which is unknown.
3. Baly's experimental methods have often been modified during the past decade but give little confidence of value for the establishment of his theory. As "proofs" of his theory the experiments are too limited and almost entirely unconvincing.
4. Drawing definite structural or dynamic conclusions from absorption phenomena is unwise; grounding a comprehensive chemical theory on the same is too speculative to serve any useful purpose.

SEATTLE, WASH.

A REPLY TO DR. DEHN.

By E. C. C. BALY.

Received October 11, 1915.

History always repeats itself. Whenever any man has been bold enough to put forward new views involving something more fundamental than the average, the Tories of the time held up their hands in horror at his daring, and his sacreligious attempt to destroy the sacred temples of their faith. Somewhat hasty in their condemnation they frequently suffer from a want of sympathetic intelligence and understanding. While very far from suggesting that Dr. Dehn in any way resembles the Tories of history I will endeavor to show that he does not quite understand and that the gift of sympathy is not his.

Dr. Dehn attacks my theory in mass formation on all sides and I am very sensible of the honor done to it. At first, however, he complains that I have modified my original views and do not speak in exactly the same language as in 1906. He even points out that I have employed new methods of work. Such criticism is not seemly from a man of science,

who no doubt himself always tries to work under the best experimental conditions and to modify his early views by help of the experience gained from many years of labor.

Turning to the theory itself as presented in my paper I ought first of all to point out (as was done in the original paper) that the development of the theory from the physical side is dealt with elsewhere. This side has fully been discussed also in a recent paper,¹ and in this paper will be found an answer to the majority of Dr. Dehn's objections.

I will restate my theory as shortly as possible. Every molecule considered in a free state has a minimum reactivity. By the supply of energy to a molecule it gains a definite reactivity, and normally speaking it must absorb that energy before it can react. The energy may be supplied by solvent, light, heat, electricity, etc. Dr. Dehn is under an entire misconception when he states that I limit the energy supply to solvent or light. I discussed these two sources in particular because I happened to have experimented with them. Each molecule when it takes in energy always absorbs it in definite amounts. After the absorption of each definite amount of energy, the molecule becomes endowed with a definite specific reactivity. Every molecule therefore can exist in definite phases according to the amounts of energy which it has absorbed. Each of these phases is characterized by a definite vibration frequency of the order of light vibrations, and thus each phase may be recognized by its own absorptive power of light of definite frequency, that is to say by its absorption band. The quantity of energy that must be absorbed by the molecule when existing in any one phase is given on the energy quantum theory by $x h \nu$, where ν is the vibration frequency characteristic of the phase of the molecule, h is the Planck constant and $x = 1, 2, 3$, etc.

From a chemical point of view therefore, if a molecule is to enter into a reaction it must absorb at least one quantum of energy ($h\nu$) and these quanta can be supplied by the solvent, by light, by heat, etc.

The above facts as regards the different vibration frequencies and the reactivities of the various molecular phases I have clearly established by experiment. Dr. Dehn falls into serious errors when he criticizes these experimental facts. He states that since concentration, temperature, etc., have marked effects on absorption bands there must be an infinite number of phases for any given molecule. Such a statement is absurd, because the effects of concentration and temperature on the wave-length of the center of the band are relatively small, while the difference between the position of the bands due to two molecular phases is very large. There is never the slightest chance of one being confused with the other.

Perhaps the most serious error Dr. Dehn has fallen into is over these

¹ *Astrophys. J.*, 42, 4 (1915).

absorption bands themselves. Had he only read my papers in the *Philosophical Magazine* or had he only studied the general question of absorption bands he would have been saved from this.

By the term absorption band is always meant an absorption band group. When Hartley, Hantzsch, Purvis, or I speak of an absorption band we always refer to the whole band group. In many cases one absorption band can be subdivided into several sub-groups, and again very frequently each sub-group can be resolved into fine absorption lines. I may say once and for all that it is the whole band group which is characteristic of the molecular phase. The fact that there are for example upwards of 400 lines composing the single ultraviolet band of benzene simply shows that there can be recognized 400 closely situated vibrations characteristic of one absorption band group and one molecular phase. Dr. Dehn goes so far as to say that this on my theory would mean 400 different molecular phases. It means nothing of the sort.

The structure of a band group and the origin of the component absorption lines is of some interest, and I think will dispel any lurking doubt on this point. The long-wave infra-red spectrum of a substance shows series of absorption bands. The frequencies of the bands in any series form consecutive multiples of a fundamental frequency. These fundamental frequencies are supposed to be rotational and are relatively small. In each series the intensities of the bands decrease as the series progresses until they become very small. When there are several series there must exist convergence frequencies and at these positions there will again be strong absorption bands, and each such convergence frequency forms the fundamental frequency of a new series, and so on. Clearly therefore the central frequencies of all the absorption band groups shown by a substance, if they belong to one series, should form consecutive multiples of a fundamental frequency. There should also be a constant difference between the central frequencies of consecutive absorption bands, and this constant difference should equal the fundamental frequency of that series.

Now I have examined many substances and in every case where the complete data are obtainable, I find this constant frequency difference between consecutive absorption bands, and, further, that this constant difference equals the frequency of an important band in the infra-red, *i. e.*, the fundamental band of the series. It is these absorption bands in the visible and ultraviolet, due to consecutive multiples of the short-wave infra-red band that forms the basis of the series, that I refer to in speaking of the characteristic vibration frequencies of the molecular phases.

To turn to the structure of any single absorption band group, Bjerrum showed that in the case of bands in the short-wave infra-red region ($\lambda = 1\mu$ to 10μ) each band consists of a single central absorption line and

that there are symmetrically distributed round it lines, the frequency of which are given by $C = nK_1$, $C = nK_2$, etc., where C is the central frequency, K_1 , K_2 , etc., are the fundamental frequencies in the deep infra-red, and $n = 1, 2, 3, 4, \dots$ etc. I have found that exactly the same holds good for the visible and ultraviolet absorption bands. This I think effectually proves that the band group is to be considered as a whole system belonging to one molecular phase.

Before leaving this physical side of the theory I think it is of some interest that where there are several fundamental series of vibrations in the deep infra-red, each series in all probability arises from a specific atom or group of atoms. Thus I have been able to calculate the absorption system of phenol from those of benzene and water, and I hope shortly, together with my friend, C. S. Garrett, to show that the vibrations of the SO_2 molecule are due entirely to the sulfur and oxygen atoms. Since the reactivity of a molecule depends on the phase it accepts, and since the phase is characterized by a free period of vibration compounded from those due to the constituent atoms, the deductions that might be drawn are suggestive.

I have laid some stress on the physical side of the theory because therein is to be found the proof that different absorption band groups and reactivities of one and the same substance are not due to molecular rearrangement as suggested by Dr. Dehn. As long as the constant frequency difference relation between them holds good all the visible and ultraviolet band groups must be functions of the same primary structure, namely, that primary structure which shows the fundamental infra-red band group.

The foregoing constitutes the fundamental basis of my theory. In order to account for the phenomena I have made use of the conception of the electromagnetic force-fields of the atom as employed by physicists to explain the Zeeman effect, and by Humphreys to explain the pressure shift of spectrum lines. By the application of these atomic force-fields to the molecule I show that all the phenomena of chemical reactivity can be explained. The first result accrues that the so-called affinity is the outward and visible sign of the mutual action of the atomic and molecular force-fields.

Certain other deductions also follow. On the one hand, we have the existence of the molecular phases, such as were foretold from the energy quantum theory; on the other, the mechanism of chemical reaction whereby an intermediate reactive phase must be accepted by any molecule before it reacts. With all due respect to my opponent this last has definitely been proven. The proof is fourfold; firstly, the change in absorption exhibited by a compound, namely, the formation of a new absorption band at the moment before a reaction takes place which dis-

appears when the reaction takes place. Secondly, the fact that the vibration frequency of the new absorption band is the same as that of the fluorescence band of the substance before the change of phase took place. Thirdly, the difference between the frequencies of the absorption band groups shown before and after the change in molecular phase is equal to the frequency of the fundamental absorption band in the infra-red, observed with the pure substance in the absence of solvent. Fourthly, the reaction will not take place at all unless the molecules pass first into the new and active phase. (The remaining deductions as regards catalysis, etc., are so obvious that they need not be referred to.)

I feel that I have said enough to answer the majority of Dr. Dehn's criticisms, namely, those which are based on misconception. No assumption is made that the necessary energy is derived from the solvent or light only. The band groups characteristic of the phases of any one molecule are few in number and can perfectly well be recognized by the constant frequency difference relation. Finally, the complete structure of a single band group as studied by Hartley, Purvis and others must not be confused with the different band groups themselves. Although one band group may consist of many hundred absorption lines, it is the whole group which is characteristic of the molecule.

The remaining criticisms may be dealt with *seriatim* as follows: Dr. Dehn says that the theory is based solely on light phenomena, and that it presents nothing new or useful. After all, the whole of astronomy is based on observations of light phenomena and indeed it is to the great work of Dr. Dehn's fellow Americans that this science owes so much. If there were nothing new in the views I put forward, I believe that Dr. Dehn would not be so troubled in spirit. When he says "nothing useful" then I fear he lacks an intelligent sympathy, for I maintain that my theory, based as it is on the force-fields of atoms so successfully employed by physicists to explain the Zeeman effect and pressure shift of spectrum lines, does make a reasoned attempt to explain many facts of chemistry which are somewhat obscure. I need only mention catalysis and those myriads of intermediate molecular compounds he refers to which are recognized but not explained by chemists.

I make no attempt to demonstrate the existence of the force-fields, but only to prove the existence of phenomena which the application of the physicists' conception of force-fields to chemical reaction leads one to expect.

Dr. Dehn again misunderstands me when he says that I assume that every change of absorption indicates a change in chemical composition. I do nothing of the sort. The change in absorption whereby a previously latent free period of vibration is called into play is due to a change in the molecular force-field produced by the addition of one or more energy

quanta supplied by light, heat or solvent, etc. The chemical composition is not changed but only the reactivity.

Dr. Dehn lastly quarrels with my use of the phrase residual affinity. He apparently views residual affinity as being only the property of molecules which are unsaturated as regards the primary valencies of the atoms composing the molecules. I plead guilty at once to the use of the phrase in a far less restricted sense. Every chemist of the present day must surely recognize the possession by compounds, saturated as regards their primary valencies, of properties which may best be classified as residual affinity. Whether these properties are attributed to secondary valencies or to any other cause, the properties exist and it is these that I speak of as residual affinity and define as the residuum of affinity which is left after the force lines of the atomic fields have condensed together with the maximum possible escape of energy. It is to this escape of energy that the heat of reaction may be traced. No chemical theory can exist without affinity although there seems to be no satisfactory definition or explanation thereof. I have ventured to show that in the electromagnetic force-fields of the atom as devised by the physicist an explanation can be found. *Hinc illae lachrymae.*

THE UNIVERSITY, LIVERPOOL.

[CONTRIBUTION FROM THE LABORATORY OF CHEMISTRY, PRINCETON UNIVERSITY.]

A CALOMEL STANDARD CELL.

BY G. F. LIPSCOMB AND G. A. HULETT.

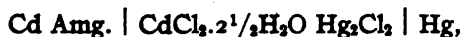
Received September 28, 1915.

Experimental investigations on standard cells have been confined mainly to two combinations, the Clark cell and the Weston cell. These have been characterized by their reproducibility and their constancy, while other combinations which have been studied have proved lacking in these characteristics. For the construction of standard cells it has been found necessary to employ liquid electrodes, owing to the inconstancy of potential shown by a metal in the solid state against a given solution, so mercury and amalgams are used. Further, it is necessary that the base metal exist in only one state of oxidation and well removed from mercury in the electromotive series. The salts of the base metals should be well defined and be quite soluble. It has been assumed that the depolarizer must possess a certain solubility which must not be too small, since mercury has shown a constant potential only against the electrolytes which contained reproducible and constant amounts of mercury in solution. This idea has been regarded as militating against the employment of mercurous chloride as depolarizer. On the other hand, if the solubility be too great, as in the case of CuSO_4 of the Daniell cell, diffusion of the depolarizer may take place, and cause inconstancy of the cell. With

mercury as cathode, the depolarizer must be a mercurous salt; and the sulfate seems best to have answered all these requirements. From the experience obtained with the Weston and Clark cells it has been found that uniformity in the size of particles of the mercurous sulfate is essential, or at least that very fine grains are to be avoided. This has been ascribed to surface tension effects influencing the solubility of the salt. The desired uniformity has been obtained by the electrolytic method of preparation, employing mercury and a solution of the acid alone.¹ This procedure obviates impurities in the product, which would occur by adsorption of the material used in the chemical preparation of the salt. Further, the presence of the relatively soluble mercuric salts in the depolarizer is reduced to a minimum by such a method of preparation.

From the experience in this laboratory, extending over some twelve years, it has been found that Weston cells containing as depolarizer gray mercurous sulfate—obtained by the electrolytic method and owing its color to finely divided mercury—have shown the greatest constancy and reproducibility. This fact may probably be explained by the reducing action which the finely divided mercury would exert on any mercuric salts which might be formed by oxygen from the solution or materials of the cell. It seemed possible, therefore, that the inconstancy of results which had hitherto been obtained in the case of "calomel electrodes" might be ascribed to the very great effect which the presence of a small quantity of mercuric salts would have on the concentration of the mercury in solution, for the concentration of the mercurous chloride in its saturated solution is exceedingly small. With finely divided mercury present, such variation should not be possible. Further, the smaller solubility of calomel, as compared with mercurous sulfate, should reduce any effect due to diffusion of the depolarizer.

Zinc chloride cannot be regarded as an easily handled, well defined, salt, owing to its hygroscopic nature, but it has been shown by Dietz² and Cohen³ that cadmium chloride forms a remarkable well defined salt with $2\frac{1}{2}$ molecules of water of crystallization. The range of stable existence extends from -10° to $+34.1^{\circ}$ and, for all ordinary purposes to which standard cells may be put, this range of temperature is amply sufficient. Its solubility, as determined by Dietz, was found to be 110 g. in 100 g. H_2O at 15° , and 120 g. in 100 g. H_2O at 25° , which was sufficiently great to fulfil the conditions requisite in standard cell work. We have therefore investigated this combination



and the results obtained and set forth in the following show a reproduci-

¹ *Phys. Rev.*, 22, 334 (1906).

² *Z. anorg. Chem.*, 20, 253 (1899).

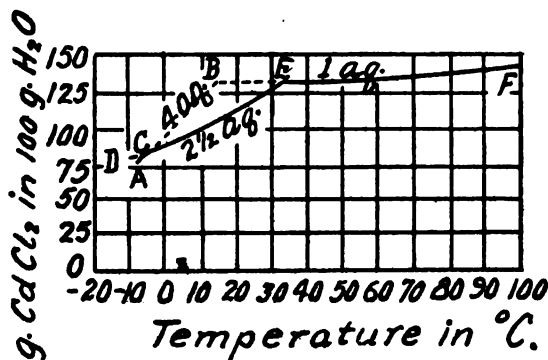
³ *Z. physik. Chem.*, 14, 73 (1894).

bility and constancy rather better than that of either of the Clark or Weston cells, both of which are liable to vary somewhat with time. We have observed these cells about nine months.

Preparation of Materials.

a. **Mercury.**—The mercury was shaken with a nitric acid solution of HgNO_3 in a separatory funnel and then distilled twice in a vacuum.

b. **Cadmium Chloride.**—A high grade cadmium chloride was brought into solution, and a small quantity of cadmium was precipitated as cadmium sulfide with hydrogen sulfide. The solution was allowed to stand for several days until the precipitate had settled. The resulting clear solution was syphoned off, and allowed to crystallize. The procedure



was adopted in order to displace any metals from solution having a lower electrolytic potential than cadmium, and in addition any of the metals with sulfides more insoluble than that of cadmium. The solution was allowed to evaporate at room temperature, and thereby large and well

formed crystals of the chloride were obtained. An analysis of a carefully dried specimen of this product yielded 19.5% of water.

The salt was therefore $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ in agreement with the observations of Dietz.¹

Calomel Electrode.

The Preparation of Calomel.—We have found that it is readily prepared electrolytically from Hg and HCl. The apparatus used for the preparation of the calomel was the same as that employed² for the preparation of mercurous sulfate, except that a tungsten wire of 2 mm. diameter, rounded to fit easily into the jar, served as cathode. The cathode remained perfectly bright throughout the operation, as tungsten does not amalgamate with mercury, while platinum does and has a slight solubility in the mercury.

Mercury to a depth of about 2 cm. was put into the jar and covered with a molar hydrochloric acid solution to a depth of 15 cm. A current density of 2 amps. per 100 sq. cm. of electrode surface was used. The product obtained was crystalline and gray in color, due to the presence of finely divided mercury. The preparation separated from the mass of

¹ *Z. anorg. Chem.*, 20, 257 (1899).

² *Phys. Rev.*, 22, 334 (1906).

mercury by stirring, decantation and the use of separatory funnel, using molar hydrochloric acid. The preparation was kept in a dark place under the acid.

Cadmium Amalgam.—A 10% cadmium amalgam was used in the construction of the cells. This amalgam was prepared by means of electrolysis, using distilled mercury and pure crystals of cadmium sulfate.

Preparation of the Paste.—A little filter was cut from filter paper with a large cork borer and fitted to a Gooch crucible. The calomel was brought into the Gooch crucible and the acid removed as completely as possible by suction; it was then washed 5 or 6 times with absolute alcohol. The absolute alcohol was next removed by washing several times with a saturated solution of cadmium chloride. For thorough washing it is best not to have the chloride in the Gooch crucible over 2 cm. deep. The washed chloride was mixed with about one-half its volume of finely powdered cadmium chloride and then the saturated solution of cadmium chloride added with stirring until a homogeneous paste was formed. The paste should be of such a consistency that it will flow from a 5 mm. glass tube.

The H type of cell was used, as it is easily filled and allows the contents of each electrode rapidly to come to the temperature of the bath. Thin walled tubing about 12 mm. in diameter was employed in their construction. The amalgam and mercury were introduced by means of a 5 mm. thin-walled glass tube about 30 cm., long drawn out at the lower end to about 3 mm. diameter. This tube was provided with a flexible rubber mouth piece and was also used for the introduction of the paste. The mercury amalgam and paste were each from 10 to 15 mm. in depth. A layer of cadmium chloride crystals about 3 mm. in depth was placed over the calomel and the amalgam. The cell was then filled to the top of the cross tube with a saturated solution of cadmium chloride, and the glass parts sealed off by using two small blast flames. The cells were arranged in supports, with lead wires so that they could readily be compared when in the bath.

Two groups of cells were made at different times, using calomel and cadmium chloride from two different preparations. These cells were placed in a thermostat regulated to 0.01° . The measurements were made by the Poggendorf compensation method, using a Broca galvanometer as zero instrument in connection with a Wolff potentiometer. The voltage could be read directly to 0.00001 V and the 6th place estimated. Weston standard cells were employed as reference. A number of these cells were available, some of them being 12 years old. The compensation current was obtained from an accumulator, the constancy of which was checked after each measurement. The voltages of

¹ *Phys. Rev.*, 22, 33.

these cells were determined at 25° over a period of several months. After this value had been established they were placed in other thermostats at 15° and 30° and their voltages measured in order to determine the temperature coefficient.

TABLE I.

		1915.						
No. of cell.	Date of constr.	Dec. 22. 1914. 25°.	Jan. 4 25°.	Jan. 25. 25°.	Feb. 12. 25°.	March 26. 25°.	April 26. 25°.	
1	Dec. 22..	0.67080	0.67080	0.67080	0.67081	0.67079	0.67080	...
2	Dec. 22..	0.67080	0.67080	0.67080	0.67080	0.67081	0.67081	...
3	Dec. 22..	0.67080	0.67080	0.67080	0.67080	0.67079	0.67080	...
		March 4.	March 9.	March 15.	May 1.	June 10.	July 12.	
4	Mar. 4...	0.67078	0.67079	0.67079	0.67079	0.67079	0.67080	...
5	Mar. 4...	0.67078	0.67080	0.67079	0.67078	0.67078	0.67079	...
6	Mar. 4...	0.67078	0.67080	0.67079	0.67078	0.67079	0.67098	...
		May 1. 25°.	June 10. 25°.	March 12. 15°.	March 15. 15°.	April 23. 30°.	April 24. 30°.	April 26. 30°.
1	Dec. 22..	0.67079	0.67080	0.67156	0.67157	0.67022	0.67044	0.67023
2	Dec. 22..	0.67080	0.67079	0.67157	0.67157	0.67022	0.67022	0.67022
3	Dec. 22..	0.67079	0.67080	0.67157	0.67157	0.67022	0.67023	0.67022

Examination of Table I will show that the combination is reproducible to the fifth decimal place and it rapidly attained a constant E. M. F. which is then steadily maintained, and no gradual decrease in E. M. F. has been noticed in any of these cells as is frequently the case with Weston cells.

Discussion of the Results.

Since the cell under consideration is capable of yielding an E. M. F. of such constancy and reproducibility, it is obvious that it may be employed to evaluate the various thermodynamic and thermochemical relations in connection with the reaction occurring in the cell. We may represent this reaction by the equation:



As is well known, the heat change accompanying a given reaction may be derived from measurements of the E. M. F. generated in a cell in which such reaction occurs. The Gibbs-Helmholtz equation connecting these factors is:

$$Q = 0.2387 nF [E + T dE/dT]$$

where

Q is the heat of reaction at temperature T° abs.

0.2387 volt coulombs = 1 cal.

E is the observed E. M. F. at temp. T° .

n the electrochemical equivalent involved in the reaction.

To evaluate this equation for Q it is necessary first to obtain the temperature coefficient of the reaction. This may be obtained in the following manner: The electromotive force at any given temperature

may be set forth as a function of the temperature of the E. M. F. at any given temperature. Thus we may set

$$E_T = E_{25} + a(T - 25) + b(T - 25)^2 + \dots$$

If the temperature range be such that higher powers of T than T^2 may be neglected, it is obvious that the values of the constants a and b in the general equation may be obtained from measurements of the E. M. F. at three temperatures. The measurements at 15° , 25° and 30° were employed to this end and the equation developed took the form:

$$E_T = 0.67080 - 0.000102(T - 25) - 0.0525(T - 25)^2$$

This equation reproduces the values at 15° and 30° C. exactly, and from it the E. M. F. at any temperature within this range may be obtained. Differentiation of this equation with respect to temperature gives the desired temperature coefficient.

Employing this equation, the E. M. F. at 18° C. was evaluated and gave $E_{18} = 0.67159$ v. while the temperature coefficient

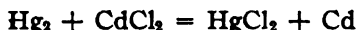
$$dT/dE = -0.000067.$$

Substitution of these values in the Gibbs-Helmholz equation gives:

$$Q_{18} = 46092[0.67159 - 291(0.000067)] = 30060 \text{ cal.}$$

The thermochemical data provide an interesting check upon the calculation.

The heat of the reaction



numerically is equal to the difference between the heat of formation of the two salts. For cadmium chloride the value given by Thomsen is 93240 cal. For mercurous chloride the most recent and reliable figure is, according to Thomsen, 63674. Hence the heat of reaction:

$$93240 - 63674 = 29566 \text{ cal.}$$

Since, however, the salt in equilibrium is the hydrated form of cadmium chloride the heat of hydration of the anhydrous salt must be taken into consideration, as well as the heat change accompanying the solution of the salt. As shown by Cohen¹ the total heat change which this involves may be represented by the general equation:

$$L_2 = m/m - w/H - w/m - w/l$$

where

m = gram mols per mol.

w = no. of mols of water of crystallization.

H = heat of hydration.

l = heat of solution of the anhydride.

L_2 = heat of formation of the hydrate.

The value of m at 18° may be obtained from the solubility data of

¹ *Z. physik. Chem.*, 34, 62 and 612 (1900).

Dietz as 9.15 g. mols water per molecule of anhydrous salt. The values for H and l were obtained from Thomsen's data as 5290 and 3010 cals., respectively. Using these data the value $L_2 = 6150$ was obtained.

Further, the heat change accompanying the solution of Cd in cadmium amalgam must also be considered. According to Cohen, this amounts to -5436 cal. per gram equivalent with 14.3% amalgam at 18° . This value was obtained from a study of the element $\text{Cd} | \text{CdSO}_4 | \text{Cd amalgam}$, which gave between 0 and 25° the voltage

$$E_t = 0.0499 - 0.000233 (t - 25).$$

This applies to amalgams containing 5 to 14% Cd. According to Hulett,¹ who had made a careful investigation of such cells, the

$$E. M. F. = 0.05175 - (0.000244) (t - 20)$$

which would give a value = 5680 cals. The total heat change, therefore, accompanying the reaction which takes place in the cell is:

$$Q = 29566 + 6150 - 5680 = 30036$$

This value shows an extraordinary agreement with that obtained from the electromotive force data, *viz.*, 30060, an agreement, indeed, well within the errors of measurement in thermochemical data.

It is obvious, therefore, that the element under consideration would form a very interesting basis for calculations according to the Nernst Heat Theorem. To this end the specific heat of the various substances are required. At the present time, however, the values for cadmium chloride appear to be lacking and the calculations must therefore be postponed until such data are forthcoming. We are undertaking work with this end in view.

In order to make the investigation of this cell more complete, unsaturated cells of the combination were constructed with a view to obtaining a cell of much smaller or zero temperature coefficient. Three groups of cells were constructed using different concentrations of cadmium-chloride solutions but none of the solid $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ was used for the paste or in the cell. The data obtained are collected in Table II.

TABLE II.

	Concentration of CdCl_2 sol. G. per 100 g. solution.	E. M. F. at 20° .	E. M. F. at 25° .	E. M. F. at 25° .
1	52 g. in 100 g. sol.....	0.67978	0.68120	0.68257
2		81	20	57
3		81	20	57
4	50 g. in 100 g. sol.....	0.68134	0.68276	0.68412
5		33	78	11
6		35	79	11
7	48 g. in 100 g. sol.....	0.68221	0.68368	0.68498
8		36	67	502

¹ *Trans. Am. Electrochem. Soc.*, 1905, 333.

The temperature coefficients of these groups at 18° were 0.000265, 0.000285, and 0.000290. From these results it is obvious that the temperature coefficient of the electromotive force of the combination changes very little with the concentration of the solution, although the voltages obtained are much higher than in the case of the saturated element.

Summary.

The possibility of employing calomel as depolarizer in the construction of precision standard cells has been established. Ordinary calomel, when suitably modified so as to contain finely divided mercury, giving the material a gray color, forms a depolarizer for cells, gives constant and reproducible electromotive forces, and this preparation should give better results in calomel electrodes.

Saturated and unsaturated cells of composition $\text{Hg} | \text{HgCl}_2 | \text{CdCl}_2 | \text{Cd}$ amalgam have been constructed, their E. M. F.'s measured and their temperature coefficients obtained.

The thermodynamics of the saturated combination has been investigated and satisfactory agreement between the heat of the reaction as calculated from the electromotive force data and that obtained from thermo-calomel measurements has been established.

PRINCETON, N. J.

SOME SOURCES OF ERROR IN VISCOSITY MEASUREMENT.

By EUGENE C. BINGHAM, H. I. SCHLESINGER AND ARTHUR B. COLEMAN.¹

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While using the viscometer recently described by Bingham,² it was observed that the viscosities (η) when calculated by the now generally accepted formula

$$\eta = Ctp - C'\rho/t \quad (1)$$

were not constant, but varied considerably when the applied pressure p was varied. In the above formula t is the time of flow, ρ the density, and C and C' are constants. As the instrument differed in what were at first considered minor details from the instrument originally successfully used by Bingham, it was thought that by its use some errors had been made apparent which might have been masked in the original viscometers and that these errors might be of such a nature as to require corrections for all viscosity measurements made in similar types of apparatus. The instrument differed from the original one in that the capillaries were rather wide so as to make possible the measurement of liquids of relatively low fluidities and, for the convenience of the manufacturer, was

¹ Part of the work reported in this article constitutes the basis of a dissertation submitted by A. B. Coleman to the faculty of the University of Chicago in part fulfillment of the requirements for the degree of Master of Science.

² *J. Ind. Eng. Chem.*, 6, 233 (1914).

provided with rather long bulbs for containing the liquid and with capillaries having ends which were somewhat trumpet-shaped. The length of the bulbs led us to examine critically the customary assumption¹ that the average pressure under which the measurement is made is one-half of the sum of the initial and the final pressures; and the presence of the trumpet-shaped openings of the capillaries seemed to demand an investigation of the kinetic energy correction which is derived on the assumption that the capillaries have square ends.² Finally, while vertical capillaries have frequently been used where relative viscosities have been determined it was thought best to make some measurements to confirm the belief that the position of the capillaries is of no importance.

As the first of the possible sources of error just named is one that can readily be investigated mathematically and which, if found to be of importance, can easily be eliminated, it will be discussed first.

While it is ordinarily assumed that the average pressure to be substituted in the viscosity formula is to be regarded as one-half the sum of the pressures at the beginning and conclusion of the viscosity measurement, a moment's reflection will make it clear to the reader that this cannot be strictly true. Thus suppose the external manometer pressure to be constant and equal to p_0 and that the hydrostatic head at the beginning is $h\rho$ and at the end $-h\rho$. Accepting the customary procedure, the average pressure would be p_0 but, as we shall see, it must strictly be less than p_0 . It is evident that when $p_0 \leq h\rho$ the flow cannot complete itself and the average pressure is not p_0 but zero. To find out to what extent the customary method of estimating the average pressure may be a source of error in viscosity measurements, a viscometer was made with a horizontal capillary having uniform bore and square ends, but the bulbs were considerably longer than those used in the ordinary form of the apparatus. The wide part of the bulbs had an estimated length of about 5.5 cm. while the constricted portions added a further 3 cm. to the distance between the marks used in estimating the volume. Measurements were made with pressures differing as widely as possible. The values given in the third column of Table I show that the product $C\eta t$ first falls slowly and then increases rapidly as the pressure becomes quite small. The viscosity, as calculated by means of Equation 1 and given in Column 5, is

¹ Cf. Brillouin, *Leçons sur la viscosité*, p. 118, et seq. Since this work was completed, the papers of Meissner (*Chem. Rev. Fett- u. Harz-Ind.*, 17, 202 (1910)) and Simeon (*Phil. Mag.*, 27, 95 (1914)) have come to the attention of the authors, in which they develop an approximate expression for the true average pressure. Neither has applied the correction except to the simplest case nor tested out the expression experimentally with fluids of varying viscosities and specific gravities. In ordinary viscometry it is important to obtain a method for making a suitable correction when the bulbs of the instrument are not simple cylinders as assumed by them.

² See Applebey, *J. Chem. Soc. (London)*, 103, 2169 (1913).

nearly constant while the pressure is large but increases rapidly as the pressure becomes small. It is apparent therefore that the difference between the assumed average pressure and the true average pressure may be the cause of the discrepancy. Our next step will therefore be to discover a method for calculating the true average pressure in order to learn how far that change will serve to correct the discrepancy.

TABLE I.—WATER AT 25° IN VISCOMETER HAVING SINGLE CAPILLARY OF UNIFORM BORE, BUT WITH BULBS APPROXIMATELY 6.0 CM. LONG.

The lack of constancy in the fifth column shows that the viscosity as ordinarily calculated (Equation 1) may be seriously in error at low pressures, but this danger may be avoided by making the proper correction (Equation 6), as shown by the constancy in the sixth column.

Press. g. per sq. cm.	Ave. t in sec.	$C\eta \times 10^6$	$C'\eta/l$	η (Eq. 1).	η (Eq. 6). $h_1 = 6.0$.
243.68	48.5	9167	236	0.00893	0.00896
201.62	58.3	9117	196	0.00892	0.00894
130.22	89.9	9080	128	0.00895	0.00897
64.57	180.1	9020	64	0.00896	0.00896
43.84	265.4	9024	44	0.00898	0.00895
26.34	446.1	9114	25	0.00909	0.00896
18.97	629.1	9256	19	0.00924	0.00895
				Av., 0.008955	

To Find the Average Pressure during the Time of Flow.—Let two vertical cylinders, Fig. 1, having the same radius r_1 be connected by means of a capillary tube of length l and radius r . A liquid whose density is ρ_1 , not corrected to *in vacuo*, stands originally at the level a in one cylinder and at d in the other. After the time t_0 has elapsed, the liquid level falls a distance h_1 from a to c in one cylinder and rises correspondingly in the other from d to f . In deriving the well-known viscosity formula

$$\eta = \frac{\pi g r^4 p t}{8 \nu l} - \frac{m n \rho_1 \nu}{8 \pi i l}, \quad (2)$$

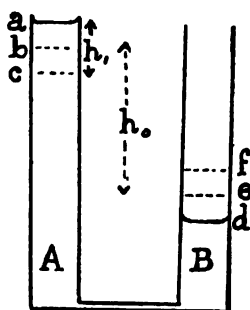


Fig. 1.

it is assumed that the pressure is constant during the time of flow. Obviously this is not the case under ordinary conditions of measurement, but as a result of experiments by Poiseuille,¹ it is generally assumed that a pressure p_0 may be employed in the formula which is equal to the pressure of a column of liquid from the level b , midway between a and c , to the corresponding level e . If this height is h_0 the applied pressure would be $h_0 \rho_1$.

But it may be noted in passing that this assumed constant applied pressure may quite as well be applied either wholly or in part outside of the viscometer. It is almost wholly external in the viscometers of Brück-

¹ *Mém. présent. par divers savants à l'academie Roy. des Scienc de l'Inst. de France*, 9, 433 (1846); cf. Brillouin, *Loc. cit.*

ner, Thorpe and Rodger, Übbelohde and others. It is entirely internal in the viscometers of Ostwald, Engler, and others. In any case the assumed constant applied pressure is

$$p_o = h_o \rho_1 + h_o' \left\{ \rho_o - \rho_o' \left(1 + \frac{h_o'}{2066} \right) + \frac{h_o'' \rho_o'}{1033} \right\} \quad (3)$$

where h_o' is the head of liquid of density ρ_o outside of the viscometer, and h_o'' is the head of air under pressure between the mean level of the liquid in the viscometer and the mean level of liquid in the manometer,¹ it being positive in value when the viscometer is below the middle of the manometer and negative when it is above, while ρ_o' is the density of the air outside of the viscometer and the normal atmospheric pressure is taken as 1033 g. per sq. cm.

We observed in Table I that the discrepancy which we are investigating occurs only when the applied pressure is small. Under these circumstances, the loss of pressure due to the kinetic energy is small, and since the correction which we desire to obtain is but a small part of the total pressure, the kinetic energy correction may be disregarded altogether in obtaining this correction. If we let x represent the distance which the liquid level has fallen after any time t , the pressure at that moment will be $p_o + h_1 \rho_1 - 2 x \rho_1$.² Equation 2 may be written

$$\pi r_1^2 dx = \frac{k}{\eta} (p_o + h_1 \rho_1 - 2 x \rho_1) dt, \quad (4)$$

where

$$k = \frac{\pi g r^4}{8 l},$$

$$t = \frac{\pi r_1^2 \eta}{2 k \rho_1} \ln \frac{p_o + h_1 \rho_1}{p_o - h_1 \rho_1 - 2 x \rho_1}.$$

The time required for a complete transpiration T is

$$T = \frac{\pi r_1^2 \eta}{2 k \rho_1} \ln \frac{p_o + h_1 \rho_1}{p_o - h_1 \rho_1} \quad (5)$$

where \ln is the natural logarithm.

To get the average pressure P , we must get the mean of the pressures during all of the equal intervals of time during which the pressure may be considered as constant. This value is

$$P = \frac{\int_0^T (p_o + h_1 \rho_1 - 2 x \rho_1) dt}{T} = \frac{2 h_1 \rho_1}{\ln \frac{p_o + h_1 \rho_1}{p_o - h_1 \rho_1}} = \frac{2}{2.303} \cdot \frac{h_1 \rho_1}{\log_{10} \frac{p_o + h_1 \rho_1}{p_o - h_1 \rho_1}} \quad (6)$$

¹ Bingham, *Loc. cit.*, p. 243.

² p_o is the apparent applied pressure as defined in the preceding paragraph.

Substituting the value of T we obtain the viscosity formula of Equation 2,

$$P = \frac{\eta}{kT} \quad (7)$$

which proves that the average pressure may be substituted into the viscosity formula. As p_0 approaches $h_1\rho_1$, the value of P approaches zero while the value of T approaches infinity. Thus is explained the peculiar increase in the viscosity as the applied pressure is lowered, as already observed in Table I. If, on the other hand, p_0 is large in comparison with $h_1\rho_1$, the average pressure P tends to approach identity with p_0 . In practice, the difference becomes less than 0.05%, *i. e.*, negligible for ordinary measurements, as soon as p_0 is thirty times as great as $h_1\rho_1$.

Where the two limbs of the viscometer are no longer cylinders, the case is not so simple. But if we conceive of the instrument as made up of a series of cylinders of varying radii as shown in Fig. 2, we can get a value for the average pressure. Let ab and ef be two narrow cylinders whose height is h_1 and whose radius is r_1 , let bc and fg be two wide cylinders whose height is h_2 and whose radius is r_2 , and let cd and gl be two narrow cylinders of height h_3 and radius r_3 . Let the difference in level between the centers of the wide cylinders be h_0 . For the sake of brevity, we assume that the flow is caused by the head of liquid within the instrument solely, and as shown in the figure, *i. e.*, $p_0 = h_0\rho_1$. During the flow through each cylinder the average pressures and the times of flow are:

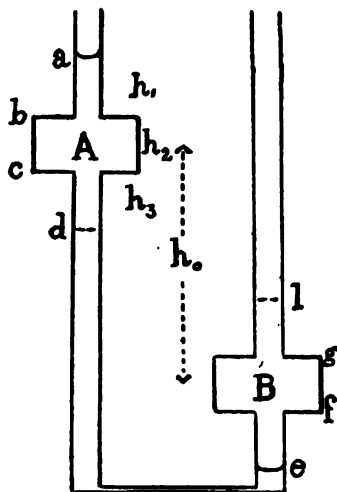


Fig. 2.

$$P_1 = \frac{2h_1\rho_1}{\ln \frac{h_0 + 2h_1 + h_2}{h_0 + h_2}}$$

$$T_1 = \frac{\eta\pi r_1^2}{2k\rho_1} \ln \frac{h_0 + 2h_1 + h_2}{h_0 + h_2}$$

$$P_2 = \frac{2h_2\rho_1}{\ln \frac{h_0 + h_2}{h_0 - h_2}}$$

$$T_2 = \frac{\eta\pi r_2^2}{2k\rho_1} \ln \frac{h_0 + h_2}{h_0 - h_2}$$

$$P_3 = \frac{2h_3\rho_1}{\ln \frac{h_0 - h_2}{h_0 - h_2 - 2h_3}}$$

$$T_3 = \frac{\eta\pi r_3^2}{2k\rho_1} \ln \frac{h_0 - h_2}{h_0 - h_2 - 2h_3}$$

Since by Equation 7

$$P = \frac{\eta\pi(r_1^2h_1 + r_2^2h_2 + r_3^2h_3)}{k(T_1 + T_2 + T_3)}$$

we have

$$P = \frac{2\rho_1(r_1^2h_1 + r_2^2h_2 + r_3^2h_3)}{r_1^2 \ln \frac{h_0 + 2h_1 + h_2}{h_0 + h_2} + r_2^2 \ln \frac{h_0 + h_2}{h_0 - h_2} + r_3^2 \ln \frac{h_0 - h_2}{h_0 - h_2 - 2h_3}}. \quad (8)$$

The average pressure becomes zero when $h_2 + 2h_3$ becomes equal to h_0 , and Equation 8 approaches identity with Equation 6 as the values of h_1 and h_3 or r_1 and r_3 becomes very small. Since Equation 8 contains the product of h times the square of r , the effect of the narrow cylinders will be especially small if both their heights and their radii are made as small as possible. Our theoretical investigation proves therefore that the bulbs of the viscometer should be as short as convenient but with a large radius. The constricted portions should be both narrow and short. These objects may be best achieved without sacrificing good drainage by having each bulb shaped like two filtering funnels placed with their wide ends together.

Finally, since the pressure $h_1\rho_1$ has no effect upon the calculated value of the viscosity unless its value amounts to one-thirtieth of p_0 , it follows that the height h_1 does not need to be known with precision. For practical purposes it seems unnecessary to use Equation 8 and the value to be used for h_1 in Equation 6 may be found by trial in the calibration of the instrument. Of course it is still more desirable to so construct the viscometer that P may be taken as equal to p_0 .

Since, as will appear, a modified Ostwald viscometer has been employed for a part of this investigation, a word may be added as to how the correction just discussed affects that instrument, in which the effective pressure is small. Let η_1 be the viscosity of the substance taken as the standard for the calibration of the instrument. Then from Equation 1,

$$\eta_1 = Cp_1t_1 - C'\rho_1/t_1.$$

In getting the true average pressure, p_1 , we use Equation 6 and we find that p_0, cp . Equation 3, becomes simply $h_0\rho_1$, so that the average pressure is

$$p_1 = \frac{2}{2.303} \frac{h_0\rho_1}{\log_{10} \frac{h_0\rho_1 + h_1\rho_1}{h_0\rho_1 - h_1\rho_1}} = K\rho_1$$

where K is a constant. Similarly, for any liquid whose viscosity, η , is unknown, the average pressure p would be $K\rho$, if ρ is its density. Hence the viscosity of any substance may be written

$$\eta = \frac{CtK\rho - c'\rho/t}{Ct_1K\rho_1 - c'\rho_1/t_1} \eta_1.$$

If the terms $C'\rho/t$ and $C'\rho_1/t_1$ are equal to zero, or if by accident their ratio is equal to the ratio of the other two terms, the equation becomes simply the Ostwald formula

$$\eta = \frac{\rho t}{\rho_1 t_1} \eta_1.$$

Any failure of the Ostwald formula is therefore due to not taking into account the loss in kinetic energy and not to any failure to recognize the true value of the average pressure.

In order to test our data, given in Table I, we have calculated the average pressures according to Equation 6 taking h_1 as equal to 6.0 cm. The values of the viscosity are given in the sixth column of the table. The divergences from the mean are less than the experimental error.

While the above test appears to be conclusive, it was noted that ρ_1 has but one value in Table I, therefore it seemed worth while to test liquids having various specific gravities, using the viscometer mentioned at the beginning of this paper as giving abnormal values. Since the two capillaries were rather large and the bulbs were very long, the instrument was well-suited for the purpose, except for the fact that the ends of the capillaries were somewhat trumpet-shaped. In this instrument the time of flow from left to right was the same as the flow from right to left within the experimental error, so that no calculation of the average resultant head was necessary. The equations were tested by measurements on the time of flow of water, 10 and 20% sugar solutions at 25° and of water, 10% sugar solution and formic acid at 18°. A temperature constancy of 0.007° was obtained by placing the instrument in an electrically regulated thermostat.

TABLE II.—WATER AT 18°.

Using water and other liquids with varying known viscosities and specific gravities, it is shown in this table and those following that reliable values of the viscosity can be calculated by means of Equations 1 and 6, since the values of C_A do not vary more than the known experimental error.

$\eta = 0.01059.$			$\rho = 0.9986.$		
1. ρ_0 g. per cc. cm.	2. T_1 sec.	3. T_2 sec.	4. $C_B \times 10^4.$	5. $C_S \times 10^4.$	6. $C_A \times 10^4.$
30.54	282.1	282.4	1.234	1.295	1.279
34.45	248.3	248.6	1.244	1.292	1.279
38.50	221.1	221.4	1.250	1.288	1.277
44.29	191.5	191.5	1.257	1.285	1.278
48.34	175.3	175.1	1.260	1.283	1.277
54.18	156.3	156.4	1.262	1.280	1.276
58.30	144.9	144.9	1.266	1.283	1.277
64.14	131.5	131.5	1.269	1.283	1.278

Av., 1.277

$h = 11.2$ cm., $h_1 = 9.78$ cm.

The data for water at 18° are given in Table II. For calculating the value of the constant C , Equations 6 and 1, the viscosity was determined

by means of a quartz viscometer of the type described by Washburn and Williams,¹ and was found to be 0.010585 based on the value of 0.008956 for the viscosity of water at 25°. This value is in good relative agreement with the results of Thorpe and Rodger. For C' , we used the value 0.01408, obtained as described by Bingham² from rough measurements of the apparatus. The fully corrected pressures are given in the first column of the table and the corresponding times of flow from right to left in the second column, the times in the reverse direction in Col. 3, the values of C^3 according to Equation 1 using the pressure p_0 instead of the true average pressure in the fourth column. The times in each case are the averages of from five to ten readings. The values of C_B are not constant, but rise continuously from the value 1.234×10^{-6} to 1.269×10^{-6} , a change of almost 3% as the pressure rises. Consequently we proceed at once to the calculation of the constant, using in the formula the true average pressure as obtained by means of Equation 6. By measurement the length of each bulb was found to be 11.2 cm. but as already pointed out, this may not be the correct value to use. As a matter of fact, the values in Col. 5, labeled C_S , are calculated using this value for h_1 , and they fall from 1.295×10^{-6} to 1.283×10^{-6} as the pressure rises. This shows that 11.2 cm. is too large, as the change in the value of the constants is in the opposite direction from what it was before the correction of the pressure was taken into consideration. In the last column of the table are found the values of the constant calculated with 9.78 cm. as the value of h_1 . The values do not vary by more than about 0.2%, which is within the range of the experimental error. The permissibility of using an arbitrary value for h_1 will become clear when it is shown that in all of the cases investigated, far better agreement is obtained with the arbitrary value than with the measured value.

In Tables III, IV, V, VI, and VII are given the data for water at 25°, for 10% sugar solution at 18° and 25° for 20% sugar solution at 25° and for formic acid at 18°. In each table the first column records the corrected pressure p_0 , the second column the average time of a large number of readings in both directions, the third column the values of C_B calculated without the use of Equation 6 for obtaining the true average pressure, the fourth column the values of C_S calculated with the use of Equation 6 taking 11.2 cm. for h_1 and the last column the values of C_A taking $h_1 = 9.78$ cm. The values for the viscosity and the density used in the calculations are given at the head of each table. In each case, the viscosity was determined by the Washburn instrument and the density by means of a density flask.

¹ THIS JOURNAL, 35, 739 (1913).

² *Loc. cit.*

³ For convenience we have called this C_B .

TABLE III.—WATER AT 25°.

ϕ , in g. per sq. cm.	$\eta = 0.008956$.	$C_B \times 10^3$.	$\rho = 0.9971$. $C_S \times 10^3$. $h_1 = 11.2$ cm.	$C_A \times 10^3$. $h_1 = 9.78$ cm.
	Ave. T in sec.			
34.71	208.6	1.248	1.291	1.280
44.55	161.2	1.259	1.287	1.279
48.50	147.8	1.262	1.284	1.279
54.47	131.5	1.265	1.282	1.280
				Av., 1.279

TABLE IV.—10% SUGAR SOLUTION AT 18°.

$\eta = 0.01432.$			$\rho = 1.0408.$	
34.62	335.3	1.237	1.286	1.275
38.53	299.3	1.246	1.286	1.276
46.40	247.4	1.252	1.279	1.274
54.33	210.4	1.259	1.278	1.275
58.25	196.1	1.260	1.276	1.275
64.19	177.5	1.264	1.278	1.275
70.25	162.4	1.264	1.275	1.274
Av., 1.275				

TABLE V.—10% SUGAR SOLUTION AT 25°.

$\eta = 0.01198.$			$\rho = 1.0377.$	
26.77	369.3	1.216	1.302	1.279
30.70	318.6	1.229	1.289	1.280
34.61	280.7	1.238	1.287	1.276
38.57	250.7	1.246	1.284	1.276
44.41	216.6	1.255	1.281	1.276
54.31	176.5	1.258	1.285	1.275
64.20	149.0	1.255	1.276	1.276
Av., 1.277				

TABLE VI.—20% SUGAR SOLUTION AT 25°.

$\eta = 0.01731.$			$\rho = 1.080.$	
44.66	310.4	1.252	1.285	1.276
54.57	252.5	1.260	1.282	1.275
64.45	213.3	1.264	1.280	1.277
74.52	184.0	1.268	1.280	1.275
84.40	162.4	1.270	1.279	1.276
92.32	148.2	1.272	1.280	1.277
Av., 1.276				

TABLE VII.—FORMIC ACID AT 18°.

$\eta = 0.01868.$			$\rho = 1.2224.$	
38.49	395.0	1.231	1.287	1.274
42.47	357.0	1.235	1.281	1.271
50.34	299.2	1.244	1.276	1.269
54.21	276.7	1.249	1.276	1.271
64.18	232.9	1.255	1.272	1.270
74.15	201.0	1.265	1.280	1.271
78.14	190.6	1.260	1.273	1.271
84.12	176.7	1.264	1.273	1.273
Av., 1.272				

The sugar solutions were made up to about the desired concentration from a Kahlbaum preparation. They were boiled to prevent the formation of moulds and were filtered until no particles were visible by transmitted light. Thus they probably are not exactly 10 or 20% solutions, nor are we absolutely certain of the purity of the sugar, but since all necessary data were determined with the solutions as used, the exact concentration is not essential. The formic acid was prepared by the method of Schlesinger and Martin¹ and was of good quality as shown by its low conductivity. The relative viscosity of the acid agrees exactly with that found by Thorpe and Rodger.

It will be seen that in no case are the values of C_B constant when calculated in the accustomed manner. On the other hand, the values of C_A obtained for water at 18° and 25° and for the sugar solutions, calculating the true average pressure, agree with one another to within 0.2%. The value obtained for formic acid at 18° is a little low—it differs from the average of the others by about 0.4%. The above data show conclusively that the so-called "applied pressure" cannot be safely used for the true "average pressure" when the change of level of the liquid within the instrument is fairly large compared with the applied pressure. How great an error the use of the latter in these calculations might have introduced is shown by the fact that had we standardized our instrument with water at 25° at a pressure of 54.47 g. per sq. cm. without regard for the correction expressed in Equation 6, the viscosity of the 10% sugar solution at 18°, calculated in the same way would have appeared to be 0.01467 instead of the correct value 0.01432. This involves an error of 2.4% in the viscosity, whereas by the use of the true average pressure in both cases the viscosity of the sugar solution is reproduced to within less than 0.25%, which is about the range of the experimental error.

Finally a short discussion of the slightly discordant value obtained for C_A when this is calculated from the data obtained with formic acid is necessary. The value obtained for this constant from the data for the acid is 1.272 while the average for the other liquids used is 1.2768. This divergency of about 0.37%, while small when compared with the error introduced by the use of the applied pressure instead of the true average pressure, is nevertheless larger than the experimental error should be. A number of possible explanations can be suggested to explain the divergency and in the following the most likely are discussed and tested:

1. The second term in Equation 2 was neglected in the derivation of the value of the true average pressure, but on account of the small relative value of this term this course seems justified.

2. The capillaries in our instrument had trumpet-shaped openings and therefore the kinetic energy correction which we employed in the calcula-

¹ THIS JOURNAL, 36, 1589 (1914).

tions may not have been correct. There are two reasons however for believing that the deviation in question is not due to an error of this sort. In the first place an error in the formula for the kinetic energy correction should have affected the constancy of C_A in the case of each of the liquids as the pressure is varied. But the tables show that no such variation can be observed even in the data for formic acid. In the second place, as will appear below, the correction when the openings of the capillary are trumpet-shaped seems to be smaller than the one we used. As the total correction amounts in maximum to only about 0.5% of the viscosity it seems quite impossible that this can be the source of the error in question.

3. The two capillaries of the instrument are vertically placed. Table IX shows that this is of no importance.

4. The most likely explanation of the difficulty is that the value which we used for the viscosity of the acid is incorrect (relatively). The relative viscosity of the acid was determined by means of a Washburn instrument and was calculated without the use of any kinetic energy correction. Based on the value 0.008956 for the viscosity of water at 25°, that of the acid at 18° was calculated to be 0.01868. This value is identical with that obtained by Thorpe and Rodger as the result of their most painstaking work. But the value which these investigators find for water is not the same as the one we use. They did not actually measure water at 25° but a value can be interpolated for this temperature either by use of their curve or their interpolation formula. The average of the two values thus obtained is 0.00892. The relative viscosity of the acid is therefore 2.094. Based on the value 0.008956 for water at 25°, which we have used as a standard, and assuming that the relative viscosity of Thorpe and Rodger is correct, the viscosity of the acid at 18° would become 0.01875. Had we used this value for the calculations of C_A , we would have obtained the value 1.276, which is in perfect agreement with the values obtained from the other liquids. While this calculation seems definitely to clear up the source of the error, we have nevertheless thought it best to investigate further the second and third points mentioned above because of the striking agreement of the relative value which we obtained with the absolute value of the viscosity of the acid as found by Thorpe and Rodger.

We may add a few remarks in regard to the older determinations of viscosity, to which the main corrections here discussed might apply. Concerning the most important work of Thorpe and Rodger, it is impossible to state whether the length of the bulbs in their instrument was small enough to render the correction for the average pressure negligible, but since they used rather large pressures, and since, according to the diagram of their instrument the distance between the marks seems fairly

small, it is very likely that their results are correct. Furthermore they used very nearly the same pressure for almost all of their measurements and the relative values would therefore in most cases be correct. Only for the very fluid substances is there reason to have doubts, because there lower pressures were employed. The results of Hosking for sugar solutions may not be so reliable, although we cannot reach a definite conclusion as his paper also fails to give the necessary data. Nevertheless Hosking's results on sugar solutions do not in the least agree with ours. We realize, to be sure, that we did not take special precautions either concerning the purity of the sugar or in regard to obtaining definitely known concentrations, but Hosking's data differ from ours more than should be caused by the points mentioned. Mr. C. Coleman, who made some measurements on sugar solutions of exactly correct concentrations, made up from an entirely different sample of sugar, obtained data in agreement with ours. It seems advisable to make a more detailed study of the older viscosity data than can be attempted here.

As has been pointed out above, one of the possible sources of error in the data with the viscometer used for the measurements on various liquids might have been due to the fact that the capillaries had trumpet-shaped ends and that therefore the kinetic energy correction may not have been correctly represented by the term $\frac{mnpV}{8\pi tL}$. This question was experi-

mentally investigated by making a viscometer in sections so that different capillaries in different positions could be used. The different sections were joined by means of short rubber tubing and, when necessary, by glass tubing also. The bulbs were short to eliminate the pressure correction above discussed, being about 1.5 cm. in length and having a capacity of approximately 3.95 cc. In order to secure good drainage, each bulb was made to approximate the shape of two cones placed base to base. The capillary used to investigate the question of the influence of trumpet-shaped ends was made by blowing a series of bulbs in an ordinary capillary tube. In this way the flow is interrupted and any loss of kinetic energy greatly increased over what it is in the ordinary form of the viscometer. The results of measurements with this capillary are shown in Table VIII.

TABLE VIII—THE EFFECT OF TRUMPET-SHAPED ENDS UPON THE KINETIC ENERGY CORRECTION. WATER AT 25°.

The lack of constancy in the values in the sixth column proves that a kinetic energy correction is necessary.

Press. corr.	Time.	$Cp \times 10^6$	$C'p/t \times 10^6$	η (Eq. 1).	η (Eq. 9).
25.14	660.7	9389	319	0.009070	0.008963
33.22	499.4	9378	423	0.008955	0.008952
54.78	303.4	9395	697	0.008698	0.008968
69.37	240.9	9446	876	0.008570	0.009017
130.54	132.9	9807	1592	0.008215	0.009361

The first column contains the pressures in grams per square centimeter after making the necessary corrections. The second column gives the times of flow in seconds. In the third and fourth columns are given the values of the different terms in the equation

$$\eta = Cpt - C'p/t. \quad (1)^1$$

Were the kinetic energy correction zero when the ends of the capillary are trumpet-shaped, this equation would become simply

$$\eta = Cpt. \quad (9)$$

We have made many measurements similar to those given above with other interrupted capillaries. In every case, the viscosity calculated by means of Equation 9² (Col. 6) seems to drop slightly at first and then rise quickly as the pressure increases. We have here used small pressures only, making the conditions advantageous for the use of Equation 9. In spite of this fact, these experiments prove that the kinetic energy correction is not negligible except over a small fraction of the range of pressures here employed. It is especially to be noted however that the viscosity as calculated by means of Equation 1 (Col. 5) is also not constant, as it should be if Equation 1 holds. We have not yet definitely determined the cause of this discrepancy. It might have resulted from the unequal diameters of the capillaries, or from having the bulbs too small to produce the theoretical dissipation of the kinetic energy. Or there remains the possibility that with the trumpet-shaped openings, the kinetic energy correction never attains its full value.

It will be seen, therefore, that our data on this point are as yet not complete. They indicate, however, that the kinetic energy correction is not entirely negligible when capillaries with trumpet-shaped ends are used, as has been suggested by Applebey,³ but that it may be smaller than when square ends are employed. In judging the deviations from the formulae, it must be born in mind that the experiments on this point were made in an apparatus which enormously exaggerated the value of the kinetic energy correction. It varies from 3.3 to 16.3% of the value of the term Cpt in Equation 1, while in most of the other experiments described herein and in viscometers as actually employed for viscosity determinations the correction seldom reaches 0.5% of the term Cpt . Consequently, even if the kinetic energy correction used in the first experiments on water, sugar, and formic acid had been too large, this error could have had but a small influence on the values of constants obtained. This conclusion, as has been stated, is borne out by the fact that for each liquid the constant was the same over a large range of pressures.

¹ *J. Ind. Eng. Chem.*, 6, 242 (1914).

² The constant in Equation 9 is of course not identical in value with the constant C in Equation 1, but is calculated independently.

³ *Loc. cit.*

Finally the effect of the position of the capillary was investigated. The instrument used for the experiments just described was employed. But in place of the capillary with the series of bulbs, we used one of uniform bore and square ends. Its length was approximately 12.75 cm. By means of the rubber tubing it could be placed either in a horizontal or in a vertical position at will. The data of Table IX are in each case the averages of several determinations with flow in alternate directions through the instrument. They show that it is immaterial whether the capillary is horizontal or inclined. They show further that where a properly constructed instrument is employed, the constants of the apparatus do not vary with the pressure and that Equation 1 can be satisfactorily used.

TABLE X.—CONSTANT OF VISCOMETER, WITH CAPILLARY HAVING SQUARE ENDS.

Press. corr.	Time.	$C \times 10^6$.	Temp.	Position of capill.
251.34	91.4	4011	25°	Horizontal
139.47	161.0	4025	25°	Horizontal
87.66	255.2	4025	25°	Horizontal
65.99	399.0	4020	25°	Horizontal
39.64	564.7	4015	25°	Horizontal
96.11	234.0	4018	25°	Vertical
75.10	185.8	4022	50°	Vertical

We reserve for a later paper a discussion of the correction for capillarity in different types of viscometers.

Conclusions.

1. The average pressure to be used in the calculation of a viscosity measurement is not strictly one-half the sum of the initial and final pressures as ordinarily assumed, and the use of this value may lead to considerable error. The method of calculating the correct value has been developed and tested experimentally.
2. In the flow of a liquid through a capillary tube it is immaterial whether the capillary is in a horizontal or in a vertical position.
3. When a liquid flows out from a capillary with a trumpet-shaped opening there is a definite loss of kinetic energy, but whether this kinetic energy correction is the same as in the well-studied case of a capillary with uniform bore, is not proved.
4. The work herein reported leads to some suggestions toward improvements in the construction of viscometers. The capillaries should have ends which are as nearly square as possible so that the kinetic energy correction may be calculable and the bulbs should be as short as possible. The latter may be accomplished by making each bulb approximate the shape of two cones placed base to base.
5. Finally in the opinion of the authors the value of using an instrument for relative as well as for absolute determinations of viscosity in

which the time of flow of any given liquid may be varied by varying the pressure has again been demonstrated by the discovery of the errors discussed.

WASHINGTON, D. C., AND CHICAGO, ILL.

THE SEPARATION OF THE RARE EARTHS GIVING THE MORE SOLUBLE DOUBLE SULFATES FROM BRAZILIAN MONAZITE SAND.

BY C. JAMES AND A. J. GRANT.

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The raw material for this work was supplied by the Welsbach Light Co. of Gloucester City, N. J., through the kindness of Dr. H. S. Miner, to whom the authors offer their most sincere thanks. It was prepared by treating the rare earth sulfates with potassium sulfate in a smaller quantity than that required for complete precipitation of the cerium metals. Under these conditions the greater part of the samarium and gadolinium, present, should remain in solution. The solution was then precipitated by oxalic acid.

The oxalates were converted into oxides by ignition. The conversion of oxalates to oxides is very troublesome when working on the large scale. The furnace used for this purpose was made by supporting a large $\frac{3}{4}$ inch steel plate in fire-brick. Coke was used as a source of heat.

The oxides were found to contain considerable quantities of lanthanum, cerium, praseodymium and neodymium in addition to samarium, gadolinium and the yttrium earths. Since the oxides dissolved in nitric acid with violence, the cerium content could not be very large.

The fractionation of the double magnesium nitrates is the best method for roughly splitting up such a mixture. The oxides were therefore dissolved in concentrated nitric acid, any ceric nitrate being reduced to the cerous condition by the addition of some of the original oxalates. The warm and somewhat diluted liquid was then filtered through large cloth filters, supported in such a way as to allow the liquid to run into a long trough which drained into a large earthenware receiver. Owing to the presence of so much of the yttrium earths, a quantity rather less than the theoretical amount of nitric acid was neutralized by powdered ignited magnesite. The solution of magnesium nitrate was diluted, and filtered in a similar manner to the rare earth nitrates. The solutions were mixed and evaporated until about half the solid crystallized out on cooling. The crystals were twice recrystallized and then placed aside, while the mother liquor was fractionated until the spectrum of samarium or erbium became intense. When the above condition had been reached the mother liquor was largely diluted and precipitated by means of oxalic acid. The oxalates were filtered off, dried and ignited to oxides. These last opera-

tions removed the large amounts of impurities, such as iron and aluminium, etc., which had accumulated in the most soluble end.

It was found advisable to arrange the double nitrates, which separated out at a period later than those first mentioned, according to the intensity of the neodymium color. The more soluble crystals were deeper colored and richer in neodymium.

After all the yttrium earths and practically the whole of the samarium had been removed, the double nitrates were again taken up and submitted to a further fractionation. As soon as the least soluble crystals became colorless or greenish they were removed from the series, while the crude neodymium magnesium nitrate was removed from the most soluble end.

The original material had, by this time, been roughly divided into three portions, as follows:

(a) Least soluble portion, forming white or greenish crystals consisting of lanthanum, cerium and praseodymium magnesium nitrates together with traces of the neodymium compound.

(b) More soluble crystals, colored deep amethyst, being largely composed of neodymium magnesium nitrate with traces of the double nitrates of magnesium with samarium, praseodymium, cerium and lanthanum.

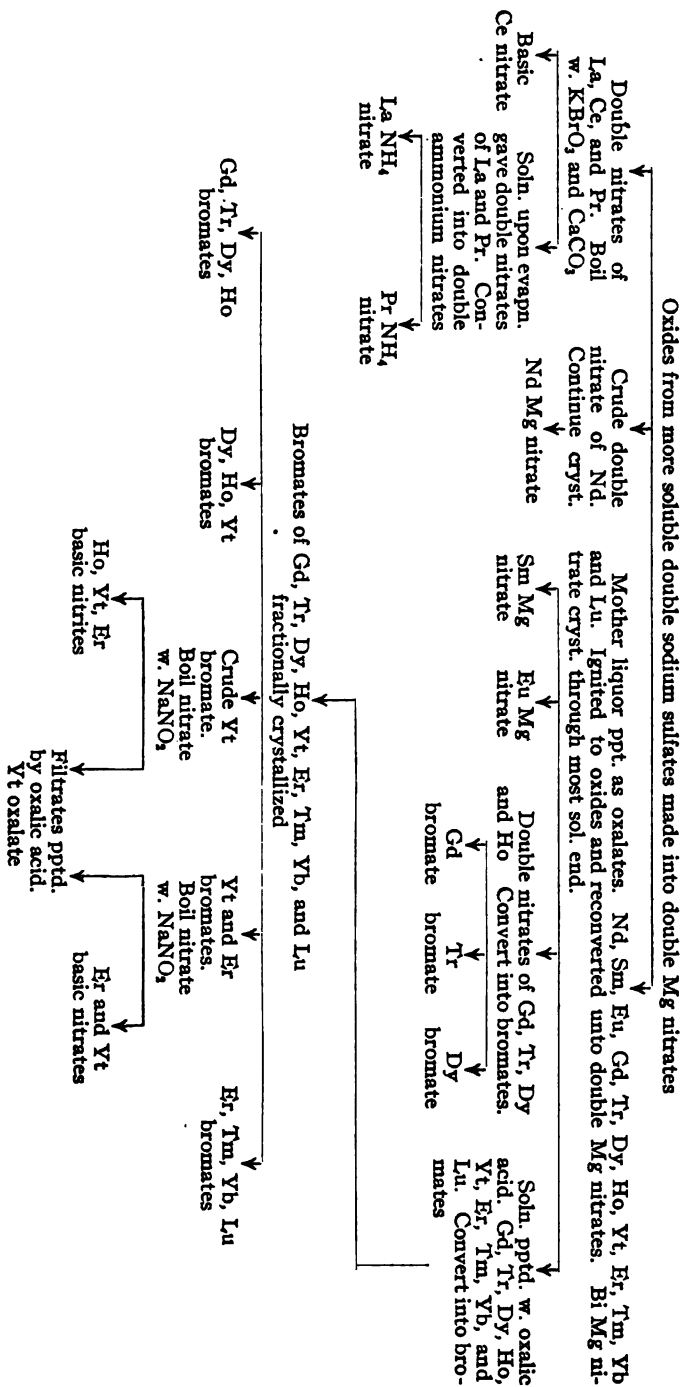
(c) Oxides from the mother liquors containing neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, yttrium, erbium, thulium, ytterbium and lutecium.

The various steps can be followed by the diagram given on p. 43.

Cerium.—This element was removed from the least soluble double nitrates by dissolving them in water, and boiling the solution with potassium bromate and powdered marble. This method has been described by James and Pratt.¹ However, there are a few conditions that must receive careful attention. The solution must not be too concentrated. It should contain about 20% of the nitrates; also the volume should be kept constant. If the liquid is allowed to evaporate too much, the increased concentration gives a cerium precipitate having colloidal tendencies. A precipitate of this kind remains suspended for a long time, and it is almost impossible to decant the supernatant liquid.

The potassium bromate was added to the boiling liquid first, and as soon as bromine vapors came off, it was gradually treated with powdered marble. When the solution of the double nitrates was inclined to be basic, it was observed that the bromate did not react for some time. At times the reaction became violent, and the liquid would froth and boil over. The addition of the marble, before the first evolution of bromine, tended to keep the solution basic. Therefore, when the boiling solution did not evolve bromine after the addition of bromate, the reaction was

¹ THIS JOURNAL, 33, 1326.



started by adding a few drops of nitric acid. This procedure never failed. When the above points were followed, the cerium was rapidly thrown down in the form of a basic ceric nitrate. This precipitate settled with extreme ease and was so dense that the supernatant liquid could be entirely poured off without stirring up the deposit. When the operation had been carefully carried out, the precipitate was of a canary yellow color. Darker colored precipitates settled much more slowly. Two operations were employed for the removal of the cerium, since the last traces usually carried down some of the other earths. The first operation was continued until no action was noticed upon adding marble. The separation of the cerium was carried out in an enamelled pail, and several of these were kept going as they required very little attention when once started. Usually, the first precipitate formed about nine-tenths of the total cerium present. After the basic ceric salt had settled, the clear supernatant liquid was poured off into a pail and a rough estimate made of the cerium remaining. If only very small quantities were present, the liquid was heated to boiling and treated with a solution of sodium peroxide. When several per cent. remained the liquid was thoroughly boiled with more powdered marble. It is not advisable to add the second precipitate to a new lot of double nitrates, since it often causes the next precipitate to form badly and to be darker colored. The basic ceric nitrate was placed in large porcelain dishes and washed by decantation with boiling water containing some nitric acid. The precipitate was finally washed upon a large Büchner funnel. It was then dissolved in hydrochloric acid, reduced by alcohol and then precipitated as the sulfate or oxalate.

The cerium free liquid, from the second basic nitrate precipitate, was evaporated until about two-thirds crystallized upon cooling. The mother liquor was found to contain practically the whole of the calcium nitrate and the excess of magnesium nitrate. Only traces of the rare earths were present. The crystals were drained and placed aside for the extraction of lanthanum and praseodymium.

The cerium forming the second precipitate may be purified by repeating the process or by employing one of many other methods that have been described by various workers.

Lanthanum.—The double magnesium nitrates, consisting mainly of the lanthanum salt, together with small amounts of praseodymium magnesium nitrate, were dissolved in water and precipitated by means of oxalic acid. The oxalates were ignited and converted into the double ammonium nitrates. These were then recrystallized many times from water containing nitric acid. The lanthanum separated in the least soluble crystals, which were obtained quite colorless.

Praseodymium was obtained from the more soluble portions obtained

during the purification of the lanthanum and from the intermediate fractions between the crude lanthanum and crude neodymium described above. Praseodymium was separated from the lanthanum by means of the double ammonium nitrates, and from neodymium by using the double magnanese nitrates. These methods have been described many times. The first having been used by Auer von Welsbach and the second by Urbain.

Neodymium.—This element was purified by the crystallization of the double magnesium nitrate.

Samarium and Europium.—The oxalates obtained from the original mother liquors were ignited to oxides. These oxides contained neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, yttrium, erbium, thulium, ytterbium and lutecium. The amount of celtium would be so small that it was not looked for. The scandium, if present, was probably lost during the precipitation as oxalates.

The oxides were converted back into double magnesium nitrates and fractionally crystallized from (1 to 1) nitric acid. Whenever the mother liquor failed to crystallize properly a considerable quantity of the double nitrate of bismuth and magnesium was added. This procedure rapidly removed the remaining europium and gadolinium. Whenever the mother liquor was considered free from the latter element it was removed and precipitated with oxalic acid. After continuing the fractionation for some time, the following main fractions were obtained: Crude neodymium magnesium nitrate; samarium magnesium nitrate; bismuth magnesium nitrate containing europium magnesium nitrate; gadolinium magnesium nitrate containing terbium, dysprosium, holmium and small amounts of yttrium; oxalates mainly yttrium but containing dysprosium, holmium, erbium, thulium, ytterbium, lutecium and traces of terbium.

Gadolinium and Terbium.—Gadolinium magnesium nitrate, containing terbium, dysprosium, holmium and small amounts of yttrium was dissolved in water and precipitated as the oxalate. The oxides obtained from the latter were dissolved in bromic acid, and the bromates, resulting, submitted to a long series of fractionation. Gadolinium appeared at the least soluble end in a very pure form. The fractions between gadolinium and dysprosium contained terbium. The solutions showed an absorption band in the blue, while the oxide was almost of a black color.

Dysprosium and Holmium.—There were two sources for these elements, the fractions of bromates more soluble than terbium, and the yttrium earth oxides obtained earlier. The oxides were converted into bromates by dissolving in bromic acid. The solution was evaporated and the crystals recrystallized fractionally from water. This gave:

(a) Least soluble-dysprosium, holmium and yttrium bromates containing traces of terbium.

(b) Bromate of yttrium containing some dysprosium and holmium.

(c) Bromate of yttrium containing very small amounts of dysprosium, holmium and erbium.

(d) Bromate of yttrium containing very small amounts of erbium.

(e) Bromates of yttrium and erbium.

(f) Bromates of erbium, thulium, ytterbium, lutecium and (celtium).

The least soluble portions of the bromates were mixed, according to their compositions, with the corresponding fractions forming the more soluble end from the terbium gadolinium series. After the fractionation had been continued again for a very long time, the terbium collected in the least soluble portion.

Dysprosium slowly separated from holmium.

The separation of dysprosium from terbium by the bromate method leaves much to be desired.

The preparation of holmium was not attempted. The separation of this element is one of the most difficult problems in inorganic chemistry.

Yttrium.—The raw material for the yttrium comprised fractions (c) and (d) of the bromates. Since these fractions were quite free from terbium, the best processes for the purification consist of the basic nitrate, the nitrite, the chromate and the cobalticyanide methods. The basic nitrate and the nitrite are the best for large amounts of material.

The basic nitrate method may be carried out several different ways. The nitrates may be fused and partially decomposed by heat. The fused mass is then carefully poured into cold water, and the whole well boiled. If the operation has been successful the entire mass goes into solution, and the basic nitrate separates upon cooling. Should the decomposition be pushed too far a residue will remain.

Many methods have been published which are based upon the basic nitrate principle, such as boiling the oxides with the nitrate solution, boiling the nitrate solution with magnesium oxide, boiling the nitrate solution with sodium hydroxide. However, it should be remembered that the best results are obtained when the basic nitrate separates from solution upon cooling.

The writers boiled a concentrated solution of the nitrates of yttrium and erbium, and added sodium hydroxide solution until crystals of the basic nitrate began to make their appearance. The liquid was then allowed to cool, and the rose colored crystals rich in erbium removed by filtration. The process was then repeated upon the filtrate, etc. The basic precipitates began to get paler as the yttrium concentrated. When the amount of erbium present was very small, the liquid did not readily clear up after the addition of the sodium hydroxide, but showed a tendency

to become colloidal. This prevented rapid filtration from the basic nitrate, and in order to avoid this, sodium nitrite was employed to render the liquid basic. Any precipitate which formed during this operation filtered easily.

When a concentrated solution of the nitrates is boiled with sodium nitrite, a basic nitrate results. In the case of a dilute solution, a basic nitrite separates as a granular precipitate during the boiling.

The yttrium was further purified by boiling the diluted nitrate solution with sodium nitrite. This gave a very pure product, which in solution showed no absorption of erbium.

The separation of erbium, lutecium, ytterbium, thulium and celtium was not attempted with this material.

DURHAM, N. H.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

OXIDATION AND REDUCTION WITHOUT THE ADDITION OF ACID.

II. THE REACTION BETWEEN STANNOUS CHLORIDE AND POTASSIUM DICHROMATE. A CONTRIBUTION TO COLLOID-CHEMISTRY.

BY MARKS NEEDLE AND JOSHUA C. WITT.

Received November 2, 1915.

It may be stated from the results of the first paper of this series that colloidal hydrous oxides or hydroxides are obtained in an oxidation-reduction reaction, in which acid must be added for the formation of normal salts, if the stoichiometric relation is the same without acid as with acid. If the reaction involves ions which are good precipitants of the colloids formed, precipitation takes place; otherwise, hydrosols are obtained.

The equation for the reaction between stannous chloride and potassium dichromate, with acid, is



where, it is seen, fourteen mols of hydrochloric acid per mol of dichromate are necessary to form the normal salts of tetravalent tin, trivalent chromium, and of potassium. The object of this investigation was to determine whether the stoichiometric relation between dichromate and stannous chloride is the same, *i. e.*, one mol of the former oxidizing three mols of the latter, and what substances are formed when no acid is added.

The Stoichiometric Relation.

Samples of commercial c. p. stannous chloride of about 0.4 g. each were rapidly transferred to beakers from a weighing bottle, dissolved in 50 cc. of water, and the solutions titrated with standard dichromate, some after adding 10 cc. of concentrated hydrochloric acid and others without the

addition of any acid. Ferrous ammonium sulfate solution containing potassium thiocyanate was employed as an outside indicator.

At first the results of the titrations without acid seemed to be slightly higher than those with acid, which, as in the titrations of ferrous sulfate with dichromate without the addition of acid, would indicate that the reaction was not instantaneous. Further investigation, however, showed that the hydrochloric acid alone gave a faint pink color with the indicator, which was caused by the ferric iron in the slightly oxidized ferrous sulfate of the indicator being brought into solution by the acid. To overcome this difficulty, the titrations in which acid was used were run until a drop of the solution gave a darker tint with the indicator than acid alone. The results with and without acid were then almost identical.

Therefore the oxidizing power of dichromate towards stannous chloride is not affected if the reaction takes place without the addition of acid. Furthermore, the reaction is practically instantaneous in dilute solutions, or, in the titrations referred to above, the results should be higher without acid than with acid.¹ It is not surprising, however, that this should be the case, for the reaction may be regarded as compounded of two, each of which has a very great velocity, namely, that between ferrous salt and dichromate and that between ferrous salt and stannous salt.

When no acid is used, stannous chloride is considerably hydrolyzed in the concentrations employed in our titrations, giving milky, opalescent, solutions. The dichromate rapidly reduced the turbidity, which disappeared after a few cubic centimeters had been added. It is also interesting to note that at the end of these titrations, the solutions possessed a peculiar, faint and yet distinct, fruity odor, which was not observed in the acid titrations. We have been unable to discover the cause of this odor. In titrating the solid salt with 0.1 *N* dichromate, an olive-green solution having no turbidity is obtained immediately.

The Products of the Reaction.

The percentage of stannous tin contained in the solid chloride was estimated by titration with 0.1 *N* dichromate in the presence of an excess of hydrochloric acid, and the amount containing an equivalent weight in grams calculated. This quantity, 119.6 g., was dissolved in about 300 cc. of water contained in a liter flask. An equivalent weight of potassium dichromate (49.03 g.), enough to completely oxidize the stannous chloride, was dissolved in 200–300 cc. of water contained in a beaker. The dichromate solution was gradually added to the stannous chloride solution, the mixture being shaken vigorously to secure homogeneity. During the process of mixing, brownish and greenish blue gelatinous masses were formed and at one point the entire mixture became a jelly; but when all the dichromate had been added a perfectly clear, deep, olive-

¹ Neidle and Witt, *THIS JOURNAL*, 37, 2356 (1915).

green solution resulted, which in sufficient depth appeared red by transmitted light, natural or artificial. The mixture was diluted to a liter and aliquot portions removed for investigation.

Treatment with Ethyl Alcohol.—One hundred cubic centimeters were evaporated to dryness on a steam bath and dried to constant weight in an air oven. The residue was treated with 95% ethyl alcohol, which dissolved all but a white crystalline substance slightly tinged with green. This alcohol-insoluble matter was filtered off by suction through a Büchner funnel and washed with 95% alcohol, but it could not be entirely freed from the slight coloration due to an adsorbed chromium compound.

Alcohol-Insoluble Matter.—The residue from 100 cc. of the original mixture was dissolved in water and made up to 250 cc. Twenty-five cubic centimeter portions were removed for the estimation of tin, chromium and chlorine. The tin was determined by precipitation with hydrogen sulfide and ignition to stannic oxide; the chromium by addition of ammonium hydroxide to the hydrogen sulfide filtrate; and the chlorine by precipitation with silver nitrate. The potassium was obtained by subtracting the amount in the alcohol-soluble matter from the total employed in the reaction.

Alcohol-Soluble Matter.—The alcohol solution was evaporated to dryness on a steam bath, and the residue, dried to constant weight in an air oven at 120°, ground and analyzed for potassium, chlorine, chromium and tin. The methods for the tin and chlorine were the same as those above, while the potassium was determined as potassium chloride, and the chromium by fusion with sodium peroxide and titrating the resulting chromate with thiosulfate.

The results calculated to totals for the entire mixture are as follows:

	Alcohol-insoluble matter.		Alcohol-soluble matter.		Total gram equiv.
	Grams.	Gram equivalents.	Grams.	Gram equivalents.	
K.....	12.11	0.3097	0.92	0.0235	0.3332
Cl.....	11.12	0.3133	19.01	0.5361	0.8494
Cr ^{III}	0.15	0.0087	17.15	0.9894	0.9981
Sn ^{IV}	0.45	0.0151	60.39	2.0300	2.0451

The quantities of the elements contained in the entire mixture are: potassium, 0.3333 equivalent; chromium, 1 equivalent; chlorine and tin, 1 and 2 equivalents, respectively, provided the stannous chloride did not contain stannic tin. It will be remembered that the weight of stannous salt containing one-half the molecular weight of unoxidized chloride was employed. The results show that 0.0451 equivalent of stannic tin was present, with which 0.0226 equivalent of chlorine was associated. Thus, the total chlorine should be 1.0226 equivalents.

It is evident that the substance separated in the alcohol treatment is potassium chloride, which therefore is one of the products of the reaction.

The constituents of the alcohol-soluble matter cannot be determined from the analysis alone. It may be observed, however, that there is a deficiency of chlorine of nearly one-sixth the total. This loss was incurred when the alcohol-soluble matter was dried in the air oven, and was due to the decomposition of stannic chloride or chromic chloride, or both.

Since no tin was lost in the process of drying, hydrated stannic chloride could not have been present to any appreciable degree, for hydrated stannic chloride volatilizes considerably when heated.¹ Hydrated chromic chloride on the other hand does yield hydrochloric acid when heated to 120° C.² We are thus led to the conclusion that the alcohol-soluble matter consists of a mixture of the hydrous oxides of tin and chromium, and hydrated chromic chloride.

If stannic chloride were a product of the reaction, it could be extracted by means of carbon bisulfide. A portion of the original mixture was evaporated to dryness on a water bath, the residue powdered, introduced into a thimble, and extracted with carbon bisulfide for about eighteen hours, but no trace of tin could be found in the solvent. Dialysis of the reaction mixture gave further evidence that it does not contain stannic chloride.

Dialysis.

Fifty cubic centimeters of the original solution were dialyzed in a parchment paper bag suspended in a beaker filled with distilled water to the level of the solution in the bag. In a short time the external liquid was colored bluish green and considerable osmosis had taken place. Fresh water was placed in the beaker every day until it was not perceptibly colored after standing twenty-four hours. The accumulated diffusate for this period was concentrated and tested for tin, but none was found, thus proving the absence of stannic chloride in the mixture.

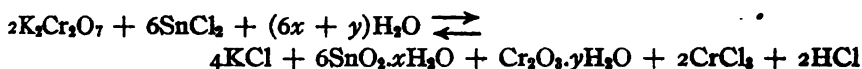
The dialysis was continued in order to free the hydrosol as far as possible from electrolytes. Excessive dilution by osmosis was avoided by keeping the level inside the membrane several centimeters higher than outside, which resulted in the concentration of the colloid as the osmosis diminished. In about five weeks when the diffusate was giving only a faint test for chloride ion, the contents of the bag set to a perfectly clear gel of a beautiful, emerald green in reflected light, and a deep red in transmitted light. In a second dialysis where no effort was made to keep the solution in the membrane from increasing in volume, 250 cc. increased to 1100 cc. in five weeks, giving a clear hydrosol resembling the

¹ *Gmelin-Kraut*, 4, I, 313.

² *Ibid.*, 3, I, 439.

hydrogel. The hydrosol may be boiled down to a very viscous consistency and on being dehydrated over sulfuric acid becomes a firm gel.

Analysis of the gel showed that it contained all the tin, practically one-half of the chromium and a negligible quantity of chlorine. These results, together with those previously obtained, enable us to formulate the reaction as follows:



Thus written the equation expresses the fact that dialysis yields a mixed hydrosol of hydrous stannic and chromic oxides in the molecular ratio of 6SnO_2 to $1\text{Cr}_2\text{O}_3$.

The reaction, with acid, is written ionically

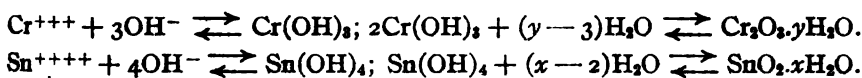


Though no acid is added in our reaction, hydrogen ion is present, due to the hydrolytic dissociation of the dichromate and stannous chloride. Equation 1, therefore, represents the reaction when no acid is added.

Aqueous solutions contain hydroxyl ion in equilibrium with hydrogen ion according to the equation:



As the hydrogen ion is removed by reaction (1) this equilibrium is disturbed, the more so as the available hydrogen is very limited and the concentration of hydroxyl ion correspondingly increases. When the latter accumulates sufficiently, the solubility products of stannic and chromic hydroxides are exceeded and the colloidal hydrous oxides are formed.



The formation of the hydrosols maintains the concentration of hydroxyl ion within perfectly definite limits, which insures a definite minimal concentration of hydrogen ion sufficient for reaction (1), which therefore continues to completion.

Other oxidation-reduction reactions without the addition of acid now being studied in this laboratory are those between ferrous chloride and potassium permanganate, ferrous chloride and hydrogen peroxide, and stannous chloride and hydrogen peroxide.

Conclusions.

1. The stoichiometric relations in the reaction between potassium dichromate and stannous chloride are the same with or without acid.
2. The products of the reaction are potassium and chromium chlorides, and stannic and chromic hydrous oxides in colloidal solution.
3. A clear mixed hydrosol of stannic and chromic hydrous oxides,

approximately in the molar ratio of 6 SnO_2 to 1 Cr_2O_3 , may be obtained by adding an equivalent amount of dichromate solution to stannous chloride and dialyzing the mixture. The hydrosol will contain all of the tin and practically one-half of the chromium used in the reaction.

4. The equations for the reaction have been formulated.

5. The work already completed as well as that now in progress on oxidation and reduction without the addition of acid justifies the conclusion that colloidal hydrous oxides are obtained in an oxidation-reduction reaction, in which acid must be added for the formation of normal salts, if the stoichiometric relations are the same with and without acid.

PITTSBURG, PA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY.]

THE ACTION OF HYDROGEN SULFIDE ON ARSENIC ACID.

By WILLIAM FOSTER.

Received August 9, 1915.

I. Introduction.

Sometime ago my colleague, Professor LeRoy W. McCay, called my attention to a paper published by Usher and Travers¹ in 1905, and entitled "The Interaction of Sulfuretted Hydrogen and Arsenic Pentoxide in Presence of Hydrochloric Acid." Inasmuch as this paper contained some statements apparently not in harmony with the results obtained by McCay years before, it seemed well worth while to conduct experiments with the view of accounting for the discrepancies existing between the authors.

Ever since the days of Berzelius there has been a difference of opinion as to the chemical changes that occur when solutions of arsenic acid or acidulated solutions of arseniates are treated with hydrogen sulfide.²

Usher and Travers repeated and confirmed Brauner and Tomicek's work in the case of dilute hydrochloric acid solutions of arsenic acid, and also extended the investigation to solutions containing up to 32% of HCl , and obtained the results given below. The experiments were carried out at about 15° , and in every case the solution contained 0.3664% of the pentoxide.

¹ *Trans.*, 87, 1370 (1905).

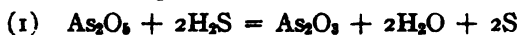
² For detailed information, the reader is referred to the following literature on the subject: Berzelius, *Ann. der Phys. u. Chem.*, 7, 2 (1826); H. Rose, *Ibid.*, 107, 186 (1859); Wackenroder, "Dictate of Forensic Chemistry," H. Ludwig, *Archiv. der Pharm.*, 2 to Reihe, 97, 32; Fuchs, *Z. anal. Chem.*, 1, 189 (1862); Bunsen, *Ann. Chem.*, 192, 305 (1878); McCay, *Am. Chem. J.*, 9, 174 (1887); *Chem. News*, 54, 287 (1886); *Am. Chem. J.*, 10, 6 (1888); *Z. anal. Chem.*, 27, 632 (1888); *Z. anorg. Chem.*, 29, 36 (1901); Brauner and Tomicek, *Trans.*, 53, 145 (1888); Neher, *Z. anal. Chem.*, 32, 45 (1893).

HCl %.	Comp. of ppt.	HCl %.	Comp. of ppt.
1.8	As ₂ S ₃ , 91 per cent.	14.34	As ₂ S ₃ , pure
7.9	As ₂ S ₃ , pure	25.10	As ₂ S ₃ , 58 per cent.
10.76	As ₂ S ₃ , pure	32.27	As ₂ S ₃ , pure

The authors also add: "The solution was contained in a flask, and sulfuretted hydrogen was slowly bubbled through the liquid at the rate of five bubbles per second. After about twelve hours, the current of gas was stopped, and the precipitate was collected, etc."

The surprising thing is, that Usher and Travers should have obtained only 91% of As₂S₃ in the most dilute hydrochloric acid used (1.8%), pure As₂S₃ in acid concentrations ranging from 7.9 to 14.34% of hydrochloric acid, and then, in stronger acid solutions, less and less pentasulfide with a corresponding increase in trisulfide.

The authors also say that the reaction between arsenic acid and hydrogen sulfide, in the presence of small concentration of hydrochloric acid, may be supposed to take place as follows:



This is the old hypothesis of Rose, and it is not in harmony with the facts.

II. Experimental.

As the result of numerous experiments the author arrived at the following conclusions:

(a) The writer agrees with McCay in the observation that arsenic acid is never reduced by hydrogen sulfide directly to arsenious acid and free sulfur according to the old hypothesis of Rose, which is still found in many text-books on chemistry.¹

(b) When a solution of arsenic acid is treated with hydrogen sulfide the compounds first interact to form monosulfoxyarsenic acid (H₂AsO₃S) as held by McCay. H₂AsO₃S is somewhat unstable. In the presence of dilute acids, it breaks down gradually into arsenious acid and sulfur; in the presence of high concentrations of acids, it is much more unstable. Concentrated hydrochloric acid brings about the decomposition *very quickly*, even at 0°. A low concentration of hydrogen sulfide also favors the breaking down of the compound. This fact, and not the hypothesis of Rose, accounts for the presence of As₂S₃ and free sulfur frequently observed in precipitates obtained by treating arsenic acid with hydrogen sulfide.

¹ The quantitative method for the determination of arsenic as the trisulfide in "Quantitative Chemical Analysis," by Fresenius-Cohn, Vol. I, pp. 415-416 (1904) is open to serious criticism on the ground that when a solution of arsenic acid is treated with hydrogen sulfide under *ordinary conditions* the precipitate is not pure arsenic trisulfide. Arsenic pentasulfide is always present in the precipitate.

(c) When solutions of arsenic acid are treated with a *rapid* stream of hydrogen sulfide no reduction takes place, even if no mineral acid be present. It was observed that *arsenic acid saturated with hydrogen sulfide yielded pure arsenic pentasulfide after the solution had stood for ninety-one hours*. It was also observed that no reduction occurred in solutions of arsenic acid in the presence of hydrochloric acid ranging in concentration from 0.9% to 32%, *i. e.*, when the solutions were treated at 15° with a *rapid* stream of hydrogen sulfide.

(d) The results of all the experiments carried out are in complete harmony with all the results formerly obtained by McCay. On the other hand, however, very few of the results agree with those obtained by Usher and Travers.¹

The conclusions summarized above are based upon the following experiments which were selected as representative of a much larger number carried out:

A. Qualitative Experiments.—(1) According to Usher and Travers, hydrogen sulfide has a marked reducing action on arsenic acid containing 1.8% of hydrochloric acid, for they obtained from such a solution a low yield (91%) of arsenic pentasulfide. To test this conclusion, a solution of arsenic acid and hydrochloric acid was prepared having approximately the strength of the solution analyzed by Usher and Travers. A little over 100 cc. of this solution were treated with 10 cc. of hydrogen sulfide water 0.0206 g. (H_2S), and allowed to stand at about 15°. Even at the end of five hours not the least turbidity was present, thus indicating that no reduction had taken place. The H_2S interacted with H_3AsO_4 to form H_4AsO_5S . The presence of H_4AsO_5S and the absence of H_2S were proved by the tests employed by McCay.² This experiment was confirmed *quantitatively* as will be shown below.

(2) A solution of H_3AsO_4 containing one volume of water to one of concentrated hydrochloric acid was treated with a *few bubbles* of H_2S , whereupon sulfur (white) separated out very quickly. On removing the free sulfur and any possible H_2S that might be present and heating the clear filtrate, more sulfur separated out. The same result was obtained in the presence of two volumes of conc. hydrochloric acid to one of water. When solutions of $Na_3AsO_5S \cdot 12H_2O$ containing the same concentrations of acid were prepared, the free sulfur removed, and the clear filtrates boiled, sulfur separated out as before.

When H_3AsO_4 was dissolved in conc. hydrochloric acid, the solution cooled to 0° and a little H_2S passed in, sulfur separated out; but on boiling the solution after the removal of free sulfur, no more sulfur separated out. The same result was also obtained at -20°. When $Na_3AsO_5S \cdot 12H_2O$

¹ *Trans.*, 87, 1370 (1905).

² *Am. Chem. J.*, 10, 6, 4 (1888).

was dissolved in conc. hydrochloric acid at 0° and -20° , respectively, the free sulfur removed, and the clear solutions boiled, no sulfur separated out.

These experiments show that H_3AsO_4 and H_2S first interact to form H_3AsO_3S , but that heat and strong hydrochloric acid break down the latter substance with the separation of sulfur. The decomposition is brought about very quickly by concentrated hydrochloric acid, even at low temperature, but the separation of sulfur is retarded in case the acid is more dilute.

B. Quantitative Experiments.—For the purpose of verifying some of the results obtained by Usher and Travers, a large number of quantitative determinations of the arsenic in solutions of arsenic acid was next made under different conditions. With this end in view, about a liter of an aqueous solution of arsenic acid was prepared, and it was found by careful analysis that 10 cc. of the solution at 25° contained 0.1751 g. As_2O_5 , which corresponds to 0.2363 g. of As_2S_5 . Portions of 10 cc. of this solution were used in the determinations described below. By properly diluting the portion measured out, a solution was obtained in each case containing approximately 0.3664% of As_2O_5 , the strength of the solution analyzed by Usher and Travers.

The arsenic in the various solutions was determined by McCay's method, *i. e.*, by heating the solutions of H_3AsO_4 and H_2S in heavy glass bottles having ground glass stoppers. The sulfide of arsenic was collected in Gooch crucibles, washed with water, followed by alcohol and carbon bisulfide to remove any free sulfur, and then dried at 110° .

(1) A rapid stream of H_2S was passed to opalescence into two portions of the solution of H_3AsO_4 containing 1.8% of HCl, followed by heating under pressure in a water bath. The following results were obtained:

Wt. of As_2S_5 : (a) 0.2363 g. (b) 0.2362 g.

As the yield of As_2S_5 was quantitative, no reduction had taken place. Almost identical results were obtained in the presence of 0.9% of HCl.

Solutions of arsenic acid containing 1.8% of HCl were introduced into two bottles, the latter joined in tandem, and H_2S passed at the rate of about one bubble a second for 31 hours; the bottles were then stoppered and allowed to stand at room temperature for about two days. The arsenic acid was then determined as usual.

Weight of precipitate: (a) 0.2352 g. (b) 0.2347 g.

The results are a little low, due to the decomposition of a small amount of the H_3AsO_3S . This conclusion was confirmed by tests made on $Na_3AsO_3 \cdot 12H_2O$, *i. e.*, it was proved that hydrochloric acid 1.8% in strength slowly splits off sulfur from H_3AsO_3S .

(2) In this experiment the H_2S was passed through the solutions under the conditions given by Usher and Travers.

After the gas had been passed through for twelve hours, the bottles were stoppered and allowed to stand for another twelve hours and then the determination of arsenic made as usual.

Weight of sulfide found: (a) 0.2370 g. (b) 0.2363 g.

The alcohol-carbon bisulfide liquid obtained by washing the precipitates were evaporated to dryness, and a negligible residue was obtained. I fail to see why Usher and Travers obtained only 91% of As_2S_3 when working under practically the same conditions.

(3) Two portions of the solution of H_3AsO_4 containing no HCl were treated to saturation with a *rapid* stream of H_2S , the bottles stoppered and allowed to stand for ninety-one hours. At the end of this period 10 cc. of conc. HCl were added to the contents of each bottle, and the arsenic determined as before.

Wt. of precipitate: (a) 0.2360 g. (b) 0.2363 g.

The conclusion is definite, therefore, that *an excess of H_2S will not reduce H_3AsO_4 , even in the course of four days.*

(4) A solution of H_3AsO_4 containing 25% of HCl was treated to saturation with a *rapid* stream of H_2S . The weight of precipitate (As_2S_3) obtained was 0.2364 g.—a quantitative yield. This agrees with the observation made by Neher.¹

Two solutions of arsenic acid were prepared containing 25% of HCl, the bottles joined in tandem, and a current of H_2S passed through at the rate of about five bubbles a second for a period of twelve hours. At the start, the first solution dissolved, of course, almost the entire amount of H_2S passing, so in the first bottle a precipitate of sulfide of arsenic made its appearance in about a minute, and in the course of five minutes a fair amount of precipitate had formed. A precipitate appeared in the second bottle in about five minutes. After the gas had passed through the solutions for twelve hours, the bottles were stoppered for another twelve hours, and the precipitate treated in the usual way.

Weights of precipitate: (a) 0.2367 g. (quantitative). (b) 0.2283 g. (8 mg. low).

There was no reduction in the case of (a), but in (b) there was a loss of considerable sulfur.

The alcohol-carbon bisulfide mixtures used in washing the precipitates were evaporated to dryness to recover any sulfur which might be in solution. In the first case the residue was negligible, while in the second case it was considerable. This was anticipated, and the explanation is clearly evident in view of all that has been said. In the second solution H_2S was received at a slower rate, and the concentration of the gas was so low, especially at the beginning of the experiment, that the H_2AsO_5S which was first formed was soon decomposed into H_3AsO_4 and sulfur, due to the high concentration of the hydrochloric acid.

¹ *Z. anal. Chem.*, 32, 45 (1893).

(5) Two solutions of arsenic acid containing 32% of HCl were treated a few minutes with a *rapid* stream of H_2S , and the determination of arsenic carried out as usual.

Weights of arsenic sulfide: (a) 0.2367 g. (b) 0.2369 g.

Again there was no reduction of arsenic acid, for the yield of As_2S_3 was quantitative.

PRINCETON, N. J.

[FROM THE DEPARTMENT OF CHEMISTRY, OHIO MECHANICS INSTITUTE.]

A THEORY OF MULTIPLE IONIZATION: A MODIFICATION OF THE ELECTROLYTIC DISSOCIATION THEORY.

I. INTRODUCTORY AND QUALITATIVE STATEMENT OF THE THEORY, WITH APPLICATIONS.¹

BY FRANCIS FARNHAM HEYROTH.

Received October 29, 1915.

In the extended application of the electrolytic dissociation theory to general and analytical chemistry which has been made and has been embodied in many textbooks, certain difficulties have been encountered. These have been satisfactorily met by making assumptions at variance with the original propositions of the theory. As such assumptions as have, from time to time, been proposed are widely scattered throughout the literature and are only occasionally alluded to in the textbooks, it seems that a comprehensive theory should be developed to embody the new conceptions as well as to show their relation to the original hypothesis.

The phenomena which the ionic theory, as it is most widely understood, fails to explain, or in regard to which further explanation is to be desired, will now be enumerated under five classes, and then a modification of the theory will be suggested which, it is hoped, will sufficiently explain most of the hitherto obscure facts.

1. We should like to have some insight into the cause of the different degrees of ionization of electrolytes. Why is one acid strong and another weak? The ionic theory offers no hypothesis to explain this.

2. There are certain types of reactions and certain compounds that seem to find no place in the theory. Such compounds are nitrosyl chloride, sulfuryl chloride, phosgene, nitrogen chloride, compounds of the halogens with each other, and practically all acid anhydrides. Nitrogen tetroxide dissolves in water to form a mixture of acids. In all the reactions of these compounds with water ionogens are formed. Are they not formed by ionic actions? Abegg² says:

¹ This paper, read before the Cincinnati Section on May 12, 1915, forms the basis of a thesis submitted to the Ohio Mechanics Institute for the Degree of Bachelor of Science.

² Abegg, "The Theory of Electrolytic Dissociation," 1907, p. 161.

"The observation that all reactions in which ions participate in measurable amounts—even the hydrolytic actions of the extremely weakly dissociated water—proceed to their equilibria with an immeasurably great velocity, has induced the assumption that indeed every capacity to react is to be attributed to the presence of ions. A basis for this assumption has been thought to exist in the fact that reactions between non-electrolytes usually proceed with extreme slowness corresponding to an immeasurably small, but not absolutely lacking, dissociation."

If this is true, the development of an ionic theory which includes them would be highly desirable.

3. The oxidizing actions of hot, concentrated sulfuric and nitric acids are not explained by the theory. The writing of the formulae of oxygen acids as hydroxides is frequently necessary in the interpretation of these reactions and has become common in the textbooks. There must be an ionic basis for these actions, although they have not yet been satisfactorily brought within the bounds of the ionic theory.

4. It is well known that only weak electrolytes obey the law of mass action.

5. **Amphoterism.**—In his "Qualitative Analysis,"¹ Stieglitz devotes an important chapter to the amphoteric electrolytes, as aluminium hydroxide. He develops, by the usual methods, equilibrium equations to show what would result if their acid and basic qualities neutralize each other.

Although amphoterism is found most prominently in the middle families of the periodic system, it is a much more common property than we usually believe it to be. Arrhenius² in his "Immuno-Chemistry" credits the albumins with being amphoteric. Some careful work in connection with the application of the ionic theory to amphoterism has been done by Winkelblech³ and by Walker,⁴ working chiefly with organic compounds, especially those in which "zwitter-ion"⁵ formation occurs. To quote Stieglitz⁶ again, "Pronounced amphoterism is shown by a large number of metal hydroxides; it is, perhaps, the rule rather than the exception." He even suggests that NaO' ions exist in immeasurable quantities in solutions of NaOH .

Theory of Multiple Ionization.—These considerations allow of but one conclusion, which may be stated in the form of a question. May not amphoterism be a property common to all electrolytes? This leads to the statement: When substances undergo electrolytic dissociation in solution they tend to dissociate into ions in at least two ways, the ratio between the different ionization constants varying from 1:1 to very nearly 1: ∞ , and depending on the nature of the solvent, the concentration of

¹ Stieglitz, "Qualitative Analysis," 1912, Theoretical Part, p. 171.

² "Immuno-Chemistry," 1907, pp. 161-3.

³ *Z. physik. Chem.*, 36, 546 (1901).

⁴ *Ibid.*, 49, 82 (1904); 57, 706 (1905).

⁵ Moore in Leffeldt's "Electro-Chemistry," 1904, Part 1, p. 145.

⁶ *Loc. cit.*

the solution and the average structure of the molecules dissociating. This forms the basis, then, of a theory of multiple ionization. For example, when nitric acid dissociates, X molecules may dissociate as follows:



Y molecules may dissociate in another manner



The familiar mathematical expression for the degree of dissociation,¹ γ , of an electrolyte is

$$\gamma = \frac{i - 1}{n - 1}.$$

Considered in the light of the theory outlined in the preceding paragraph it would be better to write it

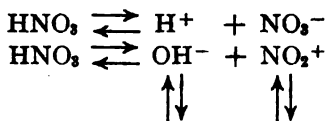
$$\alpha + \beta = \frac{i - 1}{n - 1},$$

in which α and β are the degrees of dissociation according to the two schemes of ionization which the salt, acid or base is capable of following.

Applications.—It is now necessary to apply this new hypothesis to the points outlined above in which the theory in its present form fails to give entirely satisfactory explanations.

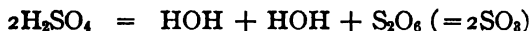
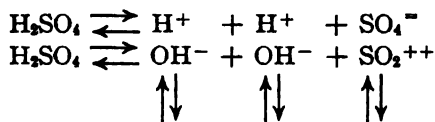
Amphoterism.—It is scarcely necessary to add anything here. Walker, Bredig, Winkelblech and others, as already mentioned, have done so much in this field that little remains to be said. They were forced to assume multiple ionization in some cases, although they did not render it broad enough to form an integral part of the theory. Stieglitz has suggested that amphoterism may account for the oxidizing action of some strong acids, although he does not seem to have fully developed the idea.

1. Dissociation of Acids and Bases.—Let us consider the equilibria in a fairly concentrated solution of nitric acid.



The result is that a series of four equilibria is set up.

For sulfuric acid we would have



¹ Arrhenius, *Z. physik. Chem.*, 1, 631 (1887).

Now for nitric acid at any given concentration we have the equilibria

$$\frac{[\text{NO}_3^-] \times [\text{H}^+]}{[\text{HNO}_3]} = K_a$$

$$\frac{[\text{NO}_2^+] \times [\text{OH}^-]}{[\text{HNO}_3]} = K_b$$

When, as in the case of aluminium hydroxide as developed by Stieglitz, the product of the concentration of H-ions and of OH-ions equal K_w , we have equilibrium. We may combine the two equations and obtain

$$\frac{[\text{NO}_3^-] \times [\text{NO}_2^+] \times K_w}{[\text{HNO}_3]^2} = K_a \times K_b$$

$$\frac{[\text{N}_2\text{O}_5]^2}{[\text{HNO}_3]^2} = \frac{K_a \times K_b}{K_w}$$

or

$$\frac{[\text{N}_2\text{O}_5]}{[\text{HNO}_3]} = \sqrt{\frac{K_a \times K_b}{K_w}}$$

The above is the ionic method of expressing the reaction between an anhydride and an oxygen acid if the acid is monobasic. For the mathematical formulation of the equilibrium between a dibasic acid, *e. g.*, sulfuric acid, and its anhydride we obtain by similar reasoning the equation

$$\frac{2\text{SO}_3}{\text{H}_2\text{SO}_4} = \frac{1}{K_w} \sqrt{K_a \times K_b}$$

In the above examples we note that when the two types of acid radicals unite, the anhydride or its polymer is formed. It is interesting to note in this connection that the anhydride of H_2SO_4 exists in two modifications, one of which has the molecular formula SO_3 and the other S_2O_5 . This affords us a new definition of an inorganic anhydride: An anhydride of an oxygen acid is an oxide which, in aqueous solution, is more or less completely hydrolyzed by water, due to its dissociation into two oxide radicals, oppositely charged, which combine with the ions of water to form the acid. A more striking definition would be: An acid anhydride is a salt formed by the self-neutralization of an acid.

A strong acid is usually understood to be one which, at a definite concentration, contains a relatively great concentration of H-ions, while a weak acid is one whose ionization constant is such that at the same concentration it will yield fewer H-ions. A low concentration of H-ions is the result of one or both of two causes: either only a small concentration of H-ions results from the ionization of the acid, which would be the case when the acid is only slightly ionized, or a greater number of H-ions are formed, some of which are removed immediately after formation. The latter might be the result of multiple ionization. Most of the OH ions

formed by the basic ionization of the acid would be removed by some of the H-ion formed by the acid ionization as relatively un-ionized water. So we see that multiple ionization may be one cause of the weakness of acids, and whenever it does occur must tend to lower the H-ion concentration of the acid and so be one of the factors which give the ionization constant a definite value. If the number of molecules of an hydroxide dissociating as a base exceeds the number dissociating as an acid we have a base. Let A represent the number of molecules of an hydroxide dissociating as an acid and B, the number dissociating as base. Then the limits between which an hydroxide may have acid properties at infinite dilution are $A = 1$, $B = 0$, and $A = B$. For basic properties the limits are $A = 0$, $B = 1$, and $A = B$.

Viewed in this light, determinations of the relative strengths of acids and bases by conductivity measurements are bound to be erroneous because the velocities of the ions formed by the hitherto unassumed modes of ionization are not taken into account. In his work on amphoteric electrolytes, J. Walker pointed out that, in calculating the conductance of an amphoteric electrolyte at infinite dilution, we must obtain the sum of the products of four ions into their specific conductances, and not two as is usually done. The different velocities of the ions may be such that the error is either large or small. In weak acids and bases the errors will probably be greatest, while in the strongest acids they will be insignificant, since these acids ionize, practically, in only one way. To compare the values of dissociation constants obtained hydrolytically with those obtained by conductivity measurements is very interesting. When all ionic velocities concerned are known, this may afford a method for the determination of the prevalence of multiple ionization.

If we apply these conceptions to non-oxygen acids we arrive at conclusions similar to those reached by the chemists who are elaborating electronic theories. H. S. Fry¹ formulates the ionization of hydrochloric acid exactly as the theory here advanced would lead us to formulate it.

It is unnecessary here to apply these ideas to bases, for it is obvious that such an application would present no difficulties. It is assumed that solutions of ammonium hydroxide ionize either as is usually believed, or as follows: $\text{NH}_3 \rightleftharpoons \text{NH}_2^- + \text{H}^+$. This explains how it attaches the NH_2 group to mercury salts, something which cannot be explained unless multiple ionization is assumed.

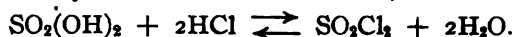
The next step is to find an underlying cause for the fact that some molecules tend to ionize in only one way, while others tend to break up in more ways than one. One theory is stereochemical. All molecules of a compound do not necessarily possess the same structure. Some may have a structure which would influence them to ionize as an acid,

¹ H. S. Fry, *THIS JOURNAL*, 23, 263 (1914).

while the structure of others might lead to their basic ionization. On the relative amounts of these molecules in a solution might depend the strength of that solution as acid or base. Electronic theories, as those recently developed by W. A. Noyes,¹ L. W. Jones² and Fry³ might be of assistance.

This theory explains in a very simple manner why silver and mercury oxides and not hydroxides are precipitated by NaOH. If any of these hydroxides should be formed in solution, they would yield by their acid and basic ionization some Ag^+ and AgO^- ions. These ions, being oppositely charged, would at once combine to form dissolved silver oxide. But as this is insoluble, while the hydroxide is not insoluble, it will at once be precipitated and this will continue until only a little dissolved silver hydroxide is left.

2. The second point outlined near the beginning of this paper was that a number of inorganic reactions involving ionogens did not find a place in the ionic theory. From what has gone before it is reasonable to suppose that sulfuryl chloride is formed in exceedingly small quantities when strong sulfuric and hydrochloric acids are mixed,



This is the first time we have encountered the case where the basic qualities of one acid are neutralized by another acid. So the theory of multiple ionization rationalizes the existence of the inorganic acid chlorides and the analogous anhydrides. It may even be possible to prepare compounds of this type which are not yet known. This offers a wide field for profitable research. The reaction between nitrogen tetroxide and water probably takes place in two different ways at the same time. Some molecules ionize as NO^+ and NO_3^- and these react with water to give HNO_3 and $\text{NO}(\text{OH})$. Others ionize, yielding NO_2^+ and NO_2^- which react with water to give HNO_2 and $\text{NO}_2(\text{OH})$.

3. **Oxidizing Action of Acids.**—In attempting to explain oxidation-reduction reactions in terms of direct transfers of electric charges between atoms and their ions, Stieglitz⁴ has suggested that oxidizing acids, as permanganic, nitric, arsenic, etc., owe their power to their capacity to ionize minimally as bases. In terms of the theory we have just developed, the oxidizing action of nitric acid is due to its basic dissociation: $\text{HNO}_3 \rightleftharpoons \text{NO}_2^+ + \text{OH}^-$. The NO_2^+ ion has a definite solution tension and may pass off as a brown gas after surrendering its charge to any other atom or ion which will hold it more firmly, just as Cu^{++} gives its charges to zinc

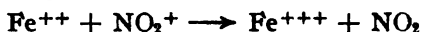
¹ W. A. Noyes, *THIS JOURNAL*, 34, 663 (1912); 35, 767 (1913).

² L. W. Jones, *Am. Chem. J.*, 50, 414 (1913).

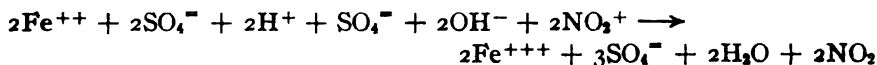
³ Fry, *THIS JOURNAL*, 30, 34 (1908); 34, 664 (1912); 36, 262 (1914); *Z. physik. Chem.*, 76, 385 (1911).

⁴ Stieglitz, "Qualitative Chemical Analysis," 1912, I, 283.

We should expect, then, that the oxidation of a ferrous salt by concentrated nitric acid might be represented ionically as follows:



In its expanded form, we might write the equation for the action of concentrated nitric acid upon ferrous sulfate in the presence of sulfuric acid as follows:



It will be noted that it is unnecessary to consider the normal ionization of nitric acid in a qualitative discussion. If the reaction is carried out without the addition of sulfuric acid, the acid ionization of nitric acid would play the part of the sulfuric acid in the above equation.

This view of the action of nitric acid is of especial importance in organic chemistry in explaining the action of the acid in nitrations where the NO_2 group becomes attached to, *e. g.*, the benzene nucleus. It is also important to note that in performing such nitrations, a mixture of concentrated sulfuric and nitric acids is employed and this is, as Stieglitz states, of importance in facilitating the basic ionization of nitric acid.

The oxidation of NO gas by concentrated nitric acid would appear to be similar to the action of zinc on a solution of a copper salt. The NO_2^+ formed by the basic ionization of the nitric acid yields its charge to the NO molecule and passes off as a brown gas.

In the solution of copper in sulfuric acid the SO_2^{++} ions formed by the basic ionization of the acid, give up their two positive charges to the Cu, forming cupric-ion, and pass off as sulfur dioxide gas, just as H-ions give their charges to Zn when it dissolves in HCl. The oxidation of metallic aluminium to its ion by means of NaOH with evolution of H_2 is easily explained in a similar manner:



A quantitative examination of some reactions of this class will, it is hoped, form the subject of later work. An important work for the future will be the insertion of the new ions into their proper places in the electro-motive series by determining their solution tensions.

4. The most vulnerable point of the electrolytic dissociation theory as it stands is that the Ostwald dilution law does not give constant values for strong electrolytes. Repeated attempts have been made to remove this obstacle to an unqualified acceptance of the theory by many workers, particularly Jahn,¹ who with Nernst attempted to explain the anomaly by an application of Nernst's extended theory of solutions. Reactions between ions and undissociated molecules have been assumed by some

¹ *Z. physik. Chem.*, 33, 545 (1900); 35, 1 (1900); 37, 490 (1901); 38, 487 (1901); 41, 257 (1902).

to be the cause of the difficulty while Hittorf,¹ Bredig,² Noyes³ and Steele⁴ base it upon the formation of inner complexes. Abegg and Bodlander,⁵ Jones⁶ and Getman and others have attempted to explain it on the basis of hydrate formation. A mathematical formula due to Rudolphi⁷ has been transformed by Van't Hoff and Kohlrausch.⁸ A broader attempt, though still empirical, has been made by Storch.⁹ More recently important work has been done by Washburn,¹⁰ Lewis,¹¹ A. A. Noyes,¹² Kendall¹³ and others. In view of the fact that in spite of their labors, a satisfactory solution of the difficulty has never been reached, it would be decidedly out of place to even offer a suggestion without prolonged study. And yet it appears to the author that the factor of multiple ionization has hitherto been neglected. Possible effects of multiple ionization upon the so-called ionization constants, the effect of the velocities of the new ions upon the true values of degrees of dissociation at definite concentrations and the possibility of varying changes in the α and β dissociations with changing concentrations are at least worthy of the consideration of all who are interested in the question. Undoubtedly, the effects of multiple ionization, *i. e.*, oxidation, etc., are most apparent when dealing with concentrated solutions and it is also here that variations from the mass law are most pronounced.

Other Applications.—To render this introduction and general statement complete in a merely qualitative sense, it now remains to apply the hypothesis to some of the successful applications of the old theory.

Neutralization.—It is evident that neutralization may take place in more than one way in terms of the new conception. For example, the acid qualities of nitric acid may neutralize the basic qualities of sodium hydroxide or the acid qualities of sodium hydroxide may neutralize the basic qualities of nitric acid. A large number of molecules undergo the first reaction as compared with those which follow the second.

In considering neutralization an interesting confirmation of our theory is met. The Russian thermochemist Hess has shown that when an

¹ *Pogg. Ann.*, 106, 385 and 546.

² *Z. physik. Chem.*, 13, 190 (1894).

³ *THIS JOURNAL*, 36, 63 (1914).

⁴ *J. Chem. Soc.*, 82, 241 (1902).

⁵ *Z. anorg. Chem.*, 20, 453 (1897).

⁶ Monograph No. 60, Carnegie Institute.

⁷ *Z. physik. Chem.*, 17, 385 (1895).

⁸ *Ibid.*, 18, 301 and 662 (1895).

⁹ *Ibid.*, 19, 13 (1896).

¹⁰ Washburn, *THIS JOURNAL*, 33, 1686–1713, 1461–78 (1911); 35, 681–74 (1912).

¹¹ Lewis, *Ibid.*, 30, 668–83 (1910); 34, 1631–44 (1912).

¹² A. A. Noyes, *et al.*, *Ibid.*, 33, 1643, 1650, 1663, 1673, 1807, 1827 and 1836 (1911); 34, 454 (1912).

¹³ Kendall, *J. Chem. Soc.*, 101, 1275–97 (1912); *Proc. Roy. Soc.*, (A) 85, 200–19 (1912).

equivalent of a strong acid neutralizes a strong base 13,700 cal. are produced, irrespective of the strong acid or base chosen, and that with weak acids or bases less heat is produced. It now becomes clear that weak electrolytes do not give exactly this amount of heat because some of the H and OH ions formed by the weak acid or base have united before the solutions were mixed. Therefore, there is not left an equivalent of H⁺ and of OH⁻ for combination and consequently we cannot expect exactly 13,700 cal.

Hydrolysis.—This is but a continuation of the discussion of neutralization. A typical example is the neutralization of the strong base NaOH and the weak carbonic acid. This means, if the hypothesis previously advanced is tentatively accepted, that we have a base, practically all the molecules of which dissociate in one way, and an acid in which the ratio of acid to basic ionization is more nearly one to one. For example:



On the right there is an approximately equal number of H⁺ and OH⁻ ions and carbonate and carbonyl ions. On the left there are a very few NaO⁻ and H⁺ ions, and a large number of Na⁺ and OH⁻ ions. Applying the mass law, it is seen that all of the H⁺ ions would be removed as water by the relatively great number of OH⁻ ions. In order that the positive and negative charges on the remaining ions may balance, there must remain a large number of OH⁻ ions in solution. Therefore a solution of sodium carbonate reacts basic, since this is a condition of equilibrium and may be reached either by bringing together the acid and base or by dissolving the salt in water.

Summary.

1. Five points have been brought forward in which the ionic theory in its present form fails to give entirely satisfactory explanations of the observed facts, or in regard to which there may be theoretical objections.
2. To meet these points it has been suggested that ionization may take place in more ways than one. The strengths of acids and bases depend upon the relative number of molecules ionized as acid and as base. The ionic reactions between water and acid or basic anhydrides have been made clear.
3. The new hypothesis has been applied to the common reactions of neutralization and hydrolysis.

It is my endeavor to show that the hypothesis is worthy of serious consideration, and later I hope to give it quantitative examination. In conclusion, I desire to express my appreciation of the encouragement given to me by my honored friend and instructor, Dr. Sigmund Waldbott, Professor of Chemistry of the Ohio Mechanics Institute.

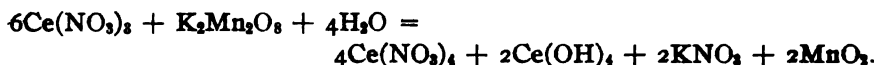
CINCINNATI, OHIO.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN.]
**THE VOLUMETRIC DETERMINATION OF CERIUM BY MEANS
 OF POTASSIUM PERMANGANATE.**

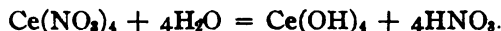
BY VICTOR LENHER AND C. C. MELOCHE.

Received December 11, 1915.

The permanganate separation of cerium from the other rare earths is based on the principle that cerium forms compounds having the valence of four in addition to the trivalent type ordinarily exhibited in the rare earths.



In addition to the formation in this first reaction of ceric hydroxide, the tetranitrate undergoes hydrolysis with the further formation of more ceric hydroxide.



The nitric acid thus liberated tends to make the reaction reversible; hence, in order to obtain complete reaction and subsequent precipitation of the cerium, this free acid must be neutralized in the proper manner.

This general reaction doubtless originated with Winkler,¹ and has been studied by a number of chemists² since that time. It has been repeatedly suggested that this principle could be applied to the determination of cerium, but few results have been published, and the conditions under which this reaction takes place have not been sufficiently emphasized. Brauner³ has stated that the method gives excellent results for the determination of trivalent cerium in the presence of tetravalent cerium.

Experimental.

Materials Employed.—For our experiments standard solutions of cerium nitrate⁴ were prepared of convenient strength, and the cerium in them was accurately determined by gravimetric means, being finally weighed in all cases as CeO_2 . The potassium permanganate solutions used were standardized against ferrous-ammonium sulfate and sodium oxalate.

Sources of Error.—If a cerous solution is rendered distinctly alkaline and the solution either heated or allowed to stand for some time, atmos-

¹ *J. prakt. Chem.*, 95, 410 (1865).

² Stolba, *Chem. Zentr.*, 10 (3 Folge), 595 (1879); Brauner, *Chem. News*, 71, 285 (1895); Drossbach, *Ber.*, 29, 3, 2453 (1896); 35, 2830 (1902); Muthmann and Rolig, *Ber.*, 31, 1719 (1898); Böhm, *Z. angew. Chem.*, 1903, 1130; Muthmann and Weiss, *Ann.*, 331, 9 (1904); Meyer and Schweitzer, *Z. anorg. Chem.*, 54, 104 (1907); James, *This Journal*, 30, 985 (1908); Roberts, *Z. anorg. Chem.*, 71, 305 (1911).

³ *Chem. News*, 71, 285 (1895).

⁴ The cerium nitrate used was courteously furnished by H. S. Miner, of the Welsbach Co.

pheric oxygen is absorbed to such an extent that the subsequent titration with potassium permanganate necessarily yields low results. This absorption of the oxygen of the air is, however, so slow that by immediately titrating, even in the cold, or by adding the most of the permanganate solution before the neutralizing agent is added, no appreciable error is introduced.

Low results may be due to occlusion. When the entire amount of neutralizing agent required is added all at once, and the cerous hydroxide precipitated before titration with the permanganate, the particles of the gelatinous precipitate are first superficially coated with the ceric hydroxide and hydrated manganese dioxide formed in the reaction, and on account of this protective coating of oxidized material, small amounts of the cerous hydroxide may escape oxidation. Low results produced in this manner may be obviated in large part by greater dilution or, still better, by adding the most of the permanganate before the neutralizing agent is introduced. A far more satisfactory procedure consists in the use of such a substance as zinc oxide, which neutralizes the free acid but does not immediately precipitate the cerous hydroxide.

In all cases it is recommended that the titration be finished hot, and that the permanency of the end point be insured by finally boiling the solution for an instant. Unless these conditions are fulfilled low results are not infrequently obtained.

The authors have not obtained results which are high, doubtless because the solutions worked with did not contain other rare earths. Others have reported high results under such conditions.

Zinc Oxide Series.—The results reported in Tables I and II were obtained by using zinc oxide as the neutralizing agent.

A measured volume of the standard cerium nitrate solutions was diluted to about 110 cc. and an excess of zinc oxide paste added. The most of the permanganate was then added in the cold, after which the solution was brought to boiling and the titration finished hot. The permanency of the end point was tested by boiling for a moment. Under these conditions a dense, granular precipitate was obtained which settled readily. The end point was sharp.

TABLE I.

Data showing the effect of zinc oxide added in the cold. 0.3026 g. Ce taken.

Ce found, g.: 0.3031; 0.3028; 0.3031; 0.3033; 0.3028.

The results shown in Table II were obtained by heating the solution to boiling before any permanganate was added.

TABLE II.¹

Data showing the effect of zinc oxide in a solution titrated at boiling temperature. 0.1630 g. Ce taken.

Ce found, g.: 0.1633; 0.1633; 0.1633, 0.1632; 0.1637; 0.1632; 0.1626; 0.1632; 0.1629; 0.1624; 0.1633; 0.1633.

¹ Results obtained by Miss Grace Van Natta.

Calcium Carbonate Series.—In the next series of experiments precipitated calcium carbonate was used as the neutralizing agent. An excess of the solid reagent was added in the form of a dry powder. The reaction in this case does not proceed with sufficient rapidity either in the cold or hot. Calcium carbonate is not as satisfactory a neutralizing agent in this titration as a number of other substances. If, however, the solution is boiled for a short time, accurate results are obtained.

TABLE III.

Data showing the influence of calcium carbonate. 0.3026 g. Ce taken.

Ce found, g.: 0.3024; 0.3035; 0.3029; 0.3026; 0.3036.

TABLE IV.

Data showing the results obtained by adding most of the permanganate before calcium carbonate was added. 0.3260 g. Ce taken.

Ce found, g.: 0.3259; 0.3258; 0.3261; 0.3258; 0.3260; 0.3254; 0.3260; 0.3261.

Magnesium Oxide Series.—Milk of magnesia was found to be one of the best neutralizing agents available for this titration. In the presence of this reagent the oxidation of the cerium by means of potassium permanganate takes place readily, even in the cold. In order to avoid the error of air oxidation, preliminary titrations were made to ascertain the approximate amount of permanganate consumed. In the titration proper, most of the permanganate is added before the magnesia is introduced. By finishing the titration hot and at the end bringing to boiling for an instant, a very sharp and satisfactory end point is obtained.

TABLE V.

Data showing the results obtained by the use of magnesia. 0.3026 g. Ce taken.

Found: 0.3024; 0.3024; 0.3022; 0.3017; 0.3024.

0.3260 g. Ce taken.

Found: 0.3262; 0.3261; 0.3261; 0.3266; 0.3265; 0.3265; 0.3260; 0.3266; 0.3263; 0.3259.

Soluble Neutralizing Agents.—When soluble compounds, such as borax, sodium carbonate, or sodium bicarbonate, were employed as the neutralizing agent, the substance was dissolved in water and a solution used. In general it may be said that a large excess of such reagents yields low results, but a slight excess does no harm. The hydrolysis taking place in the reaction itself produces potassium hydroxide from the potassium permanganate in sufficient quantity to precipitate one-third of the cerium; consequently it is only necessary to add sufficient alkali to precipitate a little more than two-thirds of the cerium. This is not the case, however, if the neutralizing agent contains a nonvolatile radical.

Borax Series.—A satisfactory neutralizing agent was found in a saturated solution of borax. This reagent possesses the added advantage that when it is used in excess no serious low errors are produced, such as invariably result when a large excess of sodium carbonate is added.

The procedure in case of soluble neutralizing agents was as follows:

30 cc. of the standard cerium solution were measured into an Erlenmeyer flask and diluted. A saturated solution of borax was gradually added with stirring until all of the cerium had been precipitated and the solution was alkaline to litmus. The solution, which then had a volume of about 110 cc., was titrated with the standard potassium permanganate. Most of the permanganate was added in the cold. The titration was finished hot, and the permanency of the end point was assured by boiling for a moment.

TABLE VI.

Data showing the results of adding borax before permanganate. 0.3026 g. Ce taken.
Ce found, g.: 0.3020; 0.3016; 0.3014; 0.3016.

TABLE VII.

Data showing the effect of adding most of the permanganate before adding borax and finishing hot. 0.1630 g. Ce taken.

Ce found, g.: 0.1628; 0.1626; 0.1626; 0.1626; 0.1624; 0.1626; 0.1626; 0.1624; 0.1627.

Sodium Bicarbonate Series.—With sodium bicarbonate as a neutralizing agent the best results are obtained when a sufficient quantity is added to precipitate at least two-thirds of the cerium. It is not necessary to render the solution alkaline to litmus at the beginning of the titration. In other respects the procedure is the same as when borax is added.

TABLE VIII.

Data showing the results obtained by adding sodium bicarbonate before permanganate.
0.3026 g. Ce taken.

Ce found, g.: 0.3013; 0.3015; 0.3009; 0.3019; 0.3010.

TABLE IX.

Data showing results obtained by the addition of most of the permanganate before the sodium bicarbonate. 0.3260 g. Ce taken.

Ce found, g.: 0.3263; 0.3262; 0.3260; 0.3261; 0.3261; 0.3263; 0.3265.

Sodium Carbonate Series.—A number of determinations were also made, using a 10% solution of sodium carbonate as a neutralizing agent. In this case, as with sodium bicarbonate, an excess of the reagent should be avoided. The amount required to precipitate about two-thirds of the cerium gives the best results. The solution will then be slightly alkaline to litmus at the end of the titration.

TABLE X.

Data showing the results obtained by the use of sodium carbonate. 0.3026 g. Ce taken.
Ce found, g.: 0.3014; 0.3016; 0.3016; 0.3014; 0.3010.

Alkaline Hydroxides.—When the fixed alkali hydroxides, sodium hydroxide and potassium hydroxide, or barium hydroxide, were introduced as neutralizing agents, low results and indistinct end points were invariably obtained.

Addition of Other Substances.—The following reagents were also tried and found to be unsuitable in this titration: sodium acetate, sodium

silicate, sodium phosphate (tribasic), disodium phosphate, sodium tungstate, and sodium arsenate.

Conclusions.

It has been shown that when cerium is titrated by means of potassium permanganate, zinc oxide or magnesium oxide are the best neutralizing agents. Fairly good results may also be obtained by using borax or sodium bicarbonate, while sodium carbonate, though yielding fair results, is still less satisfactory. The other reagents worked with are unsatisfactory so far as accurate results are concerned.

It has been shown that under proper conditions, the method is capable of giving very accurate results.

The method is also suitable for the determination of trivalent cerium in the presence of tetravalent cerium.

MADISON, WISCONSIN.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD COLLEGE.]

CHANGES IN VOLUME UPON SOLUTION IN WATER OF THE HALOGEN SALTS OF THE ALKALI METALS. II.

By GREGORY PAUL BAXTER AND CURTIS CLAYTON WALLACE.

Received November 15, 1915.

In earlier papers¹ data were given for the changes in volume upon solution in water of the chlorides, bromides and iodides of lithium, sodium and potassium at various concentrations, and by the use of these data, together with a few observations upon rubidium and caesium halides by Buchanan, a tentative hypothesis was proposed as to the reasons for the direction and magnitude of the observed effects. At the time when the earlier paper was published the desirability was evident of additional data covering wider ranges of concentration and different temperatures, as well as the examination of other salts and other solvents. In the present paper are presented new data for the halogen salts of all five alkali metals, covering nearly all concentrations from saturation down, for temperatures between 0° and either 50°, 70° or 100°.

The experimental method was in outline as follows: A weighed amount of salt was dissolved in nearly a minimum quantity of water and the volume of the solution was adjusted to a mark in a 50 cc. flask at the highest temperature employed. The flask was then cooled to room temperature and weighed. The adjusting of the volume and weighing were then carried out at several lower temperatures. Next the solution was transferred quantitatively to a 100 cc. flask and the operations were repeated at the same temperatures, beginning with the highest. Then 250 cc., 500 cc.

¹ Baxter, Boylston, Mueller, Black and Goode, *THIS JOURNAL*, 23, 901 (1911); Baxter, *Ibid.*, 23, 922 (1911).

and 1000 cc. flasks were used. From the volumes of the flasks, and the volumes of the water and salt employed, the change in volume may be calculated for each solution at each temperature. These new data duplicate the earlier results only at 25°, and at this temperature they cover wider ranges of concentration and include six new salts, the halides of rubidium and caesium.

Apparatus.

The Flasks.—These were ordinary graduated flasks, the necks of which had been constricted at the point of graduation to secure greater accuracy in setting. The minimum interior diameter of the constriction varied from about 3 mm. with the 50 cc. flask to 6 mm. with the 1000 cc. flask. The volumes of these flasks at the different temperatures were determined by finding the water content. In order to do this, after the flask had been weighed dry and empty, it was filled with water and immersed in a water thermostat long enough to ensure constant temperature. This period was in practise usually as long as two or three hours, although with the smaller flasks so long a period was really unnecessary. Constancy in the position of the meniscus was considered to indicate that the flask and contents had reached the temperature of the bath. Before the volume of the water was finally adjusted,¹ the neck of the flask was dried by aspirating air through the upper portion. The flask was then stoppered, cooled or warmed to room temperature, usually rapidly by immersion in water, cleansed and dried on the outside, and finally weighed. From the apparent weights of water the volumes were calculated by multiplying by the following factors:

0°	25°	50.04°	70.19°	100°
1.001191	1.004001	1.01316	1.02389	1.04454

the densities of water² being assumed to be at

0°	25°	50.04°	70.19°	100°
0.999868	0.997071	0.98805	0.97771	0.95838

As is to be expected, owing to the prolonged contact with water or aqueous solutions, the weights of the empty flasks slowly decreased with time. In one year the 50 cc. flask lost in weight 6 mg., the 1000 cc. flask 37 mg., and the others in proportion. Since a considerable percentage of these losses must have occurred on the outside of the flask, the change in the cubical content, owing to solution of the glass, could hardly have exceeded 0.01 cc. even with the largest flask. On the other hand, the volumes of the flasks, which were subjected to three careful standardizations at intervals of several months, seemed to show at first a perceptible

¹ The final reading was always made with the stopper of the flask removed, for the insertion of the stopper frequently produces enough pressure to alter the position of the meniscus.

² Landolt-Börnstein-Roth, "Tabellen," 1912.

increase owing, apparently, to readjustment of the glass itself at the higher temperatures. This change amounted to about 0.005 cc. in the 50 cc. flask and to about 0.05 cc. in the liter flask. In using the flasks the value obtained in the standardization nearest in point of time to the experiment was used.

The cubical coefficients of expansion of the different flasks were found to be essentially the same, and to increase slightly with rising temperature. The following table gives these values:

	25 cc. ¹	50 cc.	100 cc.	250 cc.	500 cc.	1000 cc.	Average.
70.19-50.04°	0.04311	0.0435	0.04310	0.04300	0.04321	0.04315	0.04318
50.04-25.00°	283	29	278	282	280	289	284
25.00-0.00°	290	28	294	291	273	288	286

The flasks were always weighed by substitution, the 25 cc. and 50 cc. flasks upon an ordinary analytical balance sensitive to 0.1 mg., the larger flasks on a balance sensitive to 1 mg. with a load of 1 kg. All the weights were standardized by the substitution method described by Richards.²

The Thermostats.—The thermostats were controlled by large mercury-toluene regulators which had two fingers well separated. Heat was supplied only by incandescent electric light bulbs in the 25° bath. In the 50°, 70° and 100° baths small gas flames below the baths furnished the greater part of the necessary heat, while the finer adjustment of temperature was effected by incandescent electric light bulbs controlled by the regulator. The baths were thoroughly stirred by four-inch fan propellers and were insulated by several thicknesses of asbestos paper. The baths contained distilled water except in the case of the 100° bath which was filled with concentrated calcium nitrate solution. The 0° bath was obtained by using distilled water with a large amount of washed cracked ice.

No appreciable differences in temperature could be detected in different parts of the various baths. The 0° and 25° baths remained constant within 0.01° at all times. The 50° and 70° baths were somewhat less so, but the fluctuations were never more than a few hundredths of a degree. These fluctuations could have had a perceptible effect only in the case of the larger flasks. But there the large quantity of material would respond so slowly to fluctuations that these must have been largely compensated. The 100° bath was much less satisfactory, and could not be depended upon to remain constant within less than 0.1°.

The thermometers were calibrated to hundredths of a degree by comparison with one standardized by the Physikalisch-Technische Reichsanstalt, correction being made in the usual way for exposed thread.

¹ This flask was used in work described in a subsequent paper to appear in the February number of *THIS JOURNAL*.

² *THIS JOURNAL*, 22, 144 (1900).

Purification of Materials.

The usual processes of distillation and crystallization were employed in the preparation of the pure salts and the reagents used in their preparation. *Water* was doubly distilled, once from alkaline permanganate, once from very dilute sulfuric acid with the use of tin condensers. *Nitric acid* was distilled through a platinum condenser with rejection of the first third of the distillate. Constant boiling *hydrochloric acid* was distilled through a quartz condenser. In order to eliminate chlorine, *bromine* was distilled from solution in concentrated aqueous potassium bromide. A portion of the product was converted into potassium bromide by addition to a solution of recrystallized potassium oxalate, and the remainder was distilled a second time from solution in this purer potassium bromide. Iodine was expelled from bromides made from this bromine by boiling the aqueous solutions with an excess of bromine. *Hydrobromic acid* was prepared by passing thoroughly washed hydrogen sulfide gas into the purified bromine covered with water. The solution was mechanically separated from the bromide of sulfur, and the sulfuric acid formed in the reaction was precipitated by barium hydroxide. After filtration the acid was doubly distilled with rejection of extreme fractions. Iodine was freed from chlorine and bromine by one distillation from concentrated aqueous potassium iodide. The product was washed with water and once distilled with steam. From this iodine *hydriodic acid* was prepared by reduction with thoroughly scrubbed hydrogen sulfide in the presence of much water. After the precipitated sulfur had been coagulated by heating, it was removed by filtration and the solution was freed from sulfur compounds and hydrocyanic acid by long continued boiling.

To prepare *lithium chloride*, the commercial carbonate was thoroughly washed with water and then dissolved in hydrochloric acid; a slight excess of carbonate being used to precipitate basic impurities. After the solution had been boiled and filtered, a slight excess of acid was added and the chloride was three times crystallized, twice in a quartz dish, once in platinum. In these crystallizations, and in all others, very efficient centrifugal drainage in platinum Gooch crucibles was employed.

The lithium carbonate used in making *lithium bromide* was more carefully freed from alkali metals at the start. It was first dissolved in nitric acid. The solution was boiled with an excess of carbonate and filtered, acidified with nitric acid and the salt was twice crystallized. The nitrate was now converted to carbonate by fusion in a platinum dish with four equivalents of twice crystallized oxalic acid.¹ Since the product was found to be free from both nitrate and oxalate, the carbonate was then dissolved in an excess of hydrobromic acid in a quartz dish. After the solution had been boiled and filtered, the salt was twice crystallized.

¹ Wells, *Am. Chem. J.*, 26, 265 (1891).

Lithium iodide was prepared by dissolving washed lithium carbonate in the pure hydriodic acid solution, boiling the solution with an excess of carbonate, filtering, acidifying with hydriodic acid and crystallizing. Owing to slight decomposition of lithium iodide in concentrated aqueous solution, the salt and its solutions were colored faintly yellow with a very small amount of free iodine.

C. P. sodium chloride was twice precipitated from aqueous solution in a quartz dish by conducting hydrochloric acid gas to the surface of the solution through a quartz tube. The gas was generated by boiling *c. p.* fuming acid.

To prepare sodium bromide, *sodium carbonate* was freed from impurities by three crystallizations in platinum. The carbonate was converted to oxalate by means of a slight excess of twice crystallized oxalic acid, and the oxalate to bromide by an excess of bromine which had been freed from chlorine as already described. The latter reaction was brought to completion by protracted boiling in a quartz flask. During this boiling any iodine contained originally by the bromine must have been expelled. No test for oxalate could be obtained in the solution by the addition of calcium chloride. The solution was next evaporated to dryness and fused in a platinum dish. The residue was dissolved in water, the solution was filtered and the salt was twice crystallized in platinum.

Sodium iodide was prepared from the pure sodic carbonate exactly as with the bromide. The reaction of the oxalate with iodine runs much more slowly than that with bromine, so that prolonged boiling with an excess of iodine in the quartz flask was necessary.

Potassium chloride, bromide and iodide were prepared exactly as the sodium salts, except that the starting point for the bromide and iodide was recrystallized potassium oxalate.

Merck's *rubidium chloride* was three times recrystallized from aqueous solution, the solubility of the salt being much diminished by saturating the solution with hydrochloric acid gas. The final mother liquor, when tested spectroscopically, was found to contain only very small amounts of all the other alkali metals.

The *bromide and iodide* of rubidium were prepared from the purified chloride as follows: The chloride was converted to nitrate by protracted boiling with a large excess of nitric acid in a quartz flask. Then the nitrate was mixed with four equivalents of oxalic acid and the mixture was fused in a platinum dish. The resulting carbonate was neutralized with oxalic acid and the oxalate was converted into bromide and iodide as in the cases of the corresponding salts of sodium and potassium.

We are very greatly indebted to Professor H. L. Wells, of Yale University, who kindly loaned us 200 g. of very pure caesium nitrate for preparing

the *caesium halides*. The caesium nitrate was converted to chloride by prolonged boiling in a quartz flask with continual addition of redistilled hydrochloric acid. The solution was next evaporated to dryness in a platinum dish and the caesium chloride was fused. Then the residue was dissolved, the solution was filtered and the salt twice crystallized.

To obtain the *bromide* and *iodide* of caesium the nitrate was ground with four equivalents of pure oxalic acid and the mixture was fused in a platinum dish.¹ The resulting carbonate was dissolved in a slight excess of pure hydrobromic or hydriodic acid, the solutions were evaporated to dryness and the residues were fused in a platinum dish. After solution of the residues in water and filtration, the salts were twice crystallized from aqueous solution in platinum vessels.

Preparation of the Salts for Weighing.

Especial pains were taken in drying the salts before weighing them in preparation for making up the solutions. The chlorides, with the exception of lithium chloride, were fused in a weighed platinum crucible, and the crucible and contents were weighed. Treated in this way the salts do not become appreciably basic. Since the bromides and iodides of the alkalis become somewhat basic when fused in air, these salts instead were dried without fusion. The salts were first heated for two hours in an electric air bath at 250°. Next they were powdered by gentle grinding in an agate mortar, and again were heated to 250° for two hours. After a second grinding, a suitable amount of salt was placed in a weighed platinum crucible and heated for a third period of two hours at 250°. Then the crucible with its contents was cooled and weighed. Salts when treated in this way gave essentially neutral solutions.

Since neither of the foregoing methods is applicable to the halides of lithium, both because they become decidedly basic when fused in the air and because of the hygroscopic nature of the dry salts, instead of weighing the salts, the halogen content of the most dilute solution was found by precipitation with silver nitrate and weighing the silver halide. This was done by weighing out in small flasks portions of the solution, diluting to one liter in large glass-stoppered Erlenmeyer flasks, and adding a dilute solution of a slight excess of silver nitrate containing much free acid. After coagulation by occasional shaking, the silver halide was washed by decantation and collected on a weighed platinum sponge crucible. Dilute silver nitrate solution was used in washing the silver chloride, very dilute nitric acid for the silver bromide and iodide. Finally, however, all three salts were rinsed in the crucibles with ice-cold distilled water. The crucibles and contents were dried for at least four hours at 250° before being weighed.

¹ Wells, *Loc. cit.*

Method of Procedure.

The method of conducting a series of experiments to find the change in volume during solution was as follows: A sufficient quantity of salt to prepare a very nearly saturated solution at 25° was dried as previously described. Then it was dissolved in a minimum amount of hot water and transferred to the 50 cc. flask through a funnel with a capillary stem long enough to extend through the constricted portion of the neck of the flask. In order to prevent the salt from crystallizing and clogging the capillary, the bulb of the flask and greater portion of its neck were immersed in a bath of hot water. The crucible was rinsed many times with small portions of hot water and the rinsings were transferred to the flask. If the flask was not already nearly full, it was filled to the neck (but not to the graduation) and gently agitated until the solution was homogeneous. Then it was immersed very nearly to the graduation in the thermostat at the highest temperature to be employed. When the solution had very nearly reached the temperature of the thermostat, water was added nearly to the graduation and the solution was again well agitated without wetting the neck of the flask above the graduation. Finally, the volume of the solution was adjusted exactly to the graduation by adding water slightly above the graduation and evaporating the excess of water in a current of air. If the flask was not already at 25° it was stoppered and transferred to the bath at that temperature in preparation for weighing. The outside of the flask was cleansed, usually with the use of very dilute ammonia, and after being wiped with a damp cloth, to avoid creating electrical charges, the flask was left in the balance case for one-half hour before being weighed by substitution. The empty dry flasks were always treated and weighed in a similar fashion before each series of experiments. Some difficulty was experienced from the appearance of minute bubbles on the inside of the flask when filled with solutions. These bubbles were so small and adhered so tenaciously that tapping the flask sharply was never sufficient entirely to remove them. By the use of water which had been freshly boiled in a Jena glass flask, together with sharp tapping with a glass rod it was possible to prevent the difficulty.

As soon as the flask had been filled and weighed at the highest temperature employed, the operations were repeated at the lower temperatures in succession. After the experiment at 0° had been completed the contents of the flask were quantitatively transferred to the flask next larger in size. The volume was adjusted and the solution was weighed at the same temperatures, beginning with the highest one. If, as sometimes happened, the salt began to crystallize before the lowest temperature was reached with the most concentrated solution, the whole was immediately transferred to the flask next larger in size.

In the first series of determinations with rubidium chloride at 25° ,

and with potassium chloride and lithium iodide at various temperatures, duplicate determinations were made, but since the results obtained in these experiments always lay along a smooth curve, with the other salts only one series of experiments was considered necessary.

The computation of the change in volume during solution was carried out as follows: First, the weight of salt was corrected to vacuum by adding the following vacuum corrections¹ per gram of substance:

	Cl. g.	Br. g.	I. g.
Ag.....	0.00007	0.00004	0.00007
Na.....	0.00042	0.00025	0.00019
K.....	0.00046	0.00030	0.00024
Rb.....	0.00029	0.00023	0.00021
Cs.....	0.00018	0.00013	0.00013

To correct the weight of the solution to vacuum was not always easy, for only when the volume of the solution was adjusted at 25° was the volume at the time of weighing, and hence the density, accurately known. When the volume was adjusted at a higher or at a lower temperature the method finally adopted for finding the density at room temperature was to divide the weight of the solution by the volume occupied at 25° by the water content of the flask at the temperature in question. This method assumes the same rate of expansion and contraction with the temperature for the solutions and for water. But in the more concentrated solutions, where this assumption is less nearly true, the vacuum correction is a much smaller percentage of the whole than in the less concentrated solutions which resemble water more nearly.

To find the weight of water in the solution the weight of salt corrected to vacuum is subtracted from the weight of solution corrected to vacuum.

The volume of the salt was found from the densities determined directly as described in a subsequent paper to appear in the February issue of *THIS JOURNAL* or calculated from the cubical coefficient of expansion. Since the cubical coefficient of expansion of lithium halides has not been determined, the assumption was made that these salts are not far different in this respect from the corresponding sodium salts. This assumption seems warranted since the coefficients of expansion of all the chlorides examined are nearly the same, and this is also the case for bromides and iodides. The volume of the water was computed from the weight by means of the densities given on page 78. The difference between the sum of the volumes of the salt and the water and the volume of the flask is the change in volume.

In Table III are given the data for each experiment as well as the computed change in volume per gram of salt and per gram molecule of salt. The absolute densities of the solutions also are included, although they play no part in the necessary computations. No experiments are omitted

¹ Found, except in the case of the silver salts, from the densities given on page 78.

from this table except three series known to have been made with impure water. Following the tables are curves showing change in volume during solution per gram of salt at different gram molecular concentrations. In these curves the change in volume in cubic centimeters per *gram* of salt is plotted vertically against the concentration in *mols* per liter horizontally.

It must be obvious that these curves furnish a very accurate means of computing the density of any solution of any of the salts at any temperature between the extremes. The density of the solution is equal to

$$\frac{\text{weight of solution}}{\text{volume of solution}} = \frac{\text{weight of water} + \text{weight of salt}}{\text{volume of water} + \text{volume of salt}} \\ = \text{change in volume during solution}$$

If the percentage composition is known (*i. e.*, the weights of water and salt) the volume of water, volume of salt and approximate change in volume during solution can be calculated, and thus the approximate volume of the solution. From the weight of salt and approximate volume of the solution the concentration is given nearly enough so that the exact change in volume may be found from the curves. In case the temperature in question does not correspond to any one of the curves, by plotting change in volume for the given concentration at the different temperatures, against temperature, the value for the desired temperature may be obtained. In case concentration is known at the outset (*i. e.*, weight of salt and volume of solution) there can be calculated in order: change in volume during solution, volume of salt, volume of water, weight of water and density of solution.

TABLE I.

	Sp. gr. 70.19°/4°.	Sp. gr. 50.04°/4°.	Sp. gr. 25.00°/4°.	Sp. gr. 0.00°/4°.	Cubical coeff. of expansion, 25°-50°.
NaCl.....	...	2.156	2.161	2.168	0.000106
NaBr.....	3.186 ¹	3.194	3.203	3.213	0.000119
NaI.....	...	3.653 ¹	3.665	3.677 ¹	0.000136
KCl.....	1.978	1.981	1.987	1.992	0.000117
KBr.....	...	2.740	2.749	2.756	0.000125
KI.....	...	3.114	3.123	3.133	0.000114
RbCl.....	...	2.792	2.798	2.806	0.000082
RbBr.....	...	3.340	3.349	3.358	0.000101
RbI.....	...	3.542	3.550	3.560	0.000092
CsCl.....	3.952	3.961	3.974	3.988	0.000136
CsBr.....	4.406 ¹	4.418	4.433	4.449	0.000137
CsI.....	4.480 ¹	4.493	4.509	4.525	0.000146
LiCl.....	2.059 ¹	2.063 ¹	2.068	2.073 ¹	0.00010 ²
LiBr.....	3.446 ¹	3.454 ¹	3.464	3.474 ¹	0.00012 ²
LiI.....	4.038 ¹	4.048 ¹	4.061	4.074 ¹	0.00013 ²

¹ Calculated from coefficient of expansion. See a subsequent paper to appear in the February issue of THIS JOURNAL.

² Assumed.

The weight of salt could be determined within a milligram without the least difficulty, but the accuracy in weighing the solutions diminished with increasing dilution. The weight of the 50 cc. flask and contents is probably accurate to one milligram in every case, but the weight of the 1000 cc. flask and contents is certainly not fixed more accurately than within 0.01 g., although even this represents only 0.001% in the weight of the solution. The accuracy with which the solutions were weighed obviously corresponds to an accuracy in measuring the change in volume during solution of about 0.001 cc. with the smallest, and of about 0.01 cc. with the largest flasks. That is, the change in volume was found about ten times more accurately with the smallest than with the largest flask.

TABLE II.—ANALYSES OF LITHIUM HALIDE SOLUTIONS.

All weights reduced to vacuum standard.

Salt.	Total wt. of soln. Grams.	Wt. of sample. Grams.	Wt. of silver halide. Grams.	Wt. of lithium halide in orig. soln. Grams.
LiCl.....	1017.65	50.833	4.8923	28.973
		50.930	4.9026	28.971
		50.941	4.9028	28.972
		Average, 28.972		
		969.74	50.412	2.0710
LiBr.....	1041.74	50.390	2.0705	11.787
		Average, 11.786		
		52.087	6.1275	56.680
		52.165	6.1363	56.676
		52.141	6.1338	56.679
LiI.....	1041.89	Average, 56.678		
		26.043	2.4358	55.555
		26.046	2.4360	55.556
		Average, 55.556		
		1038.36	25.941	2.2237
		25.911	2.2222	50.744
		25.928	2.2215	50.768
		Average, 50.744		

To prepare the most dilute LiCl solution, 490.45 g. were diluted to the volume of the liter flask, which therefore contained 13.963 g. of salt.

To prepare the most dilute LiBr solution, 536.50 g. were diluted to the volume of the liter flask, which therefore contained 29.190 g. of salt.

The following results are in good agreement with those previously obtained, the only differences of importance occurring where new values for the specific gravities of the solid salts are employed, as in the case of sodium bromide.

The noticeable features of the tables and curves seem to be as follows:

Lithium and cesium halides in general produce expansion during solution. Lithium chloride is the exception, but at high concentrations and temperatures between 25° and 50° even this salt produces expansion.

TABLE III.

Salt.	Temp.	Molal conc.	Wt. of salt.	Wt. of soln.	Wt. of water.	Volume of salt.	Volume of water.	Volume of soln.	Density of soln.	Change in volume, gram of salt.	Change per gram of salt.	Change per mol of salt.
LiCl.....	100.0°	11.1537	11.786	30.280	18.494	5.743	19.292	24.922	1.21495	-0.113	-0.0096	-0.27
		5.6023	..	54.328	42.542	..	44.378	49.617	1.09495	-0.504	-0.0428	-1.40
		2.7934	..	102.520	90.734	..	94.650	99.599	1.03026	-0.884	-0.0750	-2.08
		1.1219	..	245.525	233.739	..	243.846	248.332	0.99098	-1.237	-0.1050	-2.92
		0.2770	..	969.739	957.953	..	999.294	1003.377	0.96648	-1.660	-0.1410	-3.92
		6.8731	28.972	112.680	83.708	14.071	85.617	99.417	1.13341	-0.271	-0.0094	-0.40
	70.19°	2.7541	..	258.936	229.964	..	235.209	248.104	1.04366	-1.176	-0.0406	-1.72
		1.3698	..	504.576	475.604	..	486.452	498.834	1.01151	-1.689	-0.0583	-2.47
		0.6816	..	997.354	968.382	..	990.471	1002.453	0.99491	-2.089	-0.0721	-3.06
		0.3285	13.963	988.590	974.627	6.782	996.858	1002.453	0.98617	-1.187	-0.0850	-3.61
		13.7929	28.972	63.625	34.653	14.044	35.072	49.540	1.28433	+0.424	+0.0146	+0.62
		6.8774	..	113.279	84.307	..	85.327	99.355	1.14014	-0.016	-0.0006	-0.03
LiBr.....	50.04°	2.7538	..	260.875	231.903	..	234.706	247.954	1.05211	-0.796	-0.0275	-1.17
		1.3707	..	508.956	479.984	..	485.787	498.512	1.02095	-1.319	-0.0456	-1.93
		0.6821	..	1006.570	977.598	..	989.418	1001.817	1.00474	-1.645	-0.0568	-2.41
		0.3287	13.963	998.025	984.062	6.769	995.959	1001.817	0.99622	-0.911	-0.0652	-2.76
		13.8030	28.972	63.968	34.996	14.010	35.099	49.504	1.29218	+0.395	+0.0137	+0.58
		6.8822	..	113.925	84.953	..	85.203	99.286	1.14744	+0.073	+0.0025	+0.11
	25.00°	2.7577	..	262.750	233.778	..	234.465	247.779	1.06042	-0.696	-0.0240	-1.02
		1.3716	..	512.915	483.943	..	485.365	498.163	1.02961	-1.212	-0.0419	-1.78
		0.6826	..	1014.716	985.744	..	988.640	1001.094	1.01361	-1.556	-0.0537	-2.28
		0.3290	13.963	1006.263	992.300	6.752	995.215	1001.094	1.00516	-0.873	-0.0625	-2.65
		6.8872	28.972	114.437	85.465	13.975	85.476	99.213	1.15345	-0.238	-0.0082	-0.35
		2.7597	..	263.813	234.841	..	234.872	247.599	1.06549	-1.248	-0.0431	-1.83
LiBr.....	70.19°	1.3726	..	514.681	485.709	..	485.773	497.823	1.03386	-1.925	-0.0665	-2.82
		0.6831	..	1017.644	988.672	..	988.803	1000.375	1.01726	-2.403	-0.0830	-3.52
		0.3292	13.963	1008.780	994.817	6.736	994.948	1000.375	1.00840	-1.309	-0.0938	-3.98
		13.162	56.678	88.194	31.516	16.442	32.244	49.575	1.77900	+0.899	+0.0159	+1.38
		6.5635	..	136.855	80.177	..	82.006	99.417	1.37658	+0.969	+0.0171	+1.49

LiBr.....	70.19°	2.6300	..	282.703	226.025	..	231.181	248.104	1.13945	+0.481	+0.0085	+0.74
		1.3081	..	528.175	471.497	..	482.253	498.834	1.05882	+0.139	+0.0025	+0.22
		0.6509	..	1020.890	964.212	..	986.208	1002.453	1.01839	-0.197	-0.0035	-0.30
		0.3352	29.190	1001.187	971.997	8.468	994.168	1002.453	0.99874	-0.183	-0.0063	-0.55
		50.04°	13.172	56.678	88.536	31.858	16.409	49.540	1.78716	+0.887	+0.0156	+1.36
		6.5676	..	137.570	80.892	..	81.870	99.355	1.38463	+1.076	+0.0190	+1.65
		2.6316	..	284.767	228.089	..	230.847	247.954	1.14847	+0.698	+0.0123	+1.07
		1.3089	..	532.664	475.986	..	481.741	498.512	1.06851	+0.362	+0.0064	+0.55
		0.6513	..	1030.232	973.554	..	985.325	1001.817	1.02836	+0.083	+0.0015	+0.13
		0.3355	29.190	1010.717	981.527	8.451	993.394	1001.817	1.00888	-0.028	-0.0010	-0.09
		25.00°	13.181	56.678	89.014	32.336	16.362	49.504	1.79812	+0.711	+0.0125	+1.09
		6.5721	..	138.397	81.719	..	81.959	99.286	1.39392	+0.965	+0.0170	+1.48
LiI.....	70.19°	2.6335	..	286.836	230.158	..	230.834	247.779	1.15763	+0.593	+0.0103	+0.89
		1.3099	..	536.850	480.172	..	481.583	498.163	1.07766	+0.218	+0.0038	+0.33
		0.6518	..	1038.558	981.880	..	984.765	1001.094	1.03742	-0.033	-0.0006	-0.05
		0.3357	29.190	1019.059	989.869	8.427	992.777	1001.094	1.01795	-0.110	-0.0038	-0.33
		0.00°	6.5770	56.678	139.133	82.455	16.314	99.213	1.40237	+0.433	+0.0076	+0.66
		2.6354	..	288.158	231.480	..	231.511	247.599	1.16381	-0.246	-0.0043	-0.38
		1.3108	..	538.870	482.192	..	482.256	497.823	1.08245	-0.747	-0.0132	-1.14
		0.6523	..	1041.735	985.057	..	985.187	1000.375	1.04134	-1.126	-0.0199	-1.73
		0.3359	29.190	1021.738	992.548	8.402	992.679	1000.375	1.02135	-0.706	-0.0242	-2.10
		8.3718	55.556	88.894	33.337	13.764	34.097	49.575	1.79312	+1.714	+0.0309	+4.14
		4.1747	..	137.368	81.811	..	83.677	99.415	1.38176	+1.974	+0.0355	+4.75
		1.6728	..	282.800	227.243	..	232.427	248.106	1.13984	+1.915	+0.0345	+4.61
		0.8320	..	528.014	472.457	..	483.235	498.816	1.05853	+1.817	+0.0327	+4.38
50.04°	50.04°	0.4140	..	1020.514	964.957	..	986.969	1002.453	1.01802	+1.720	+0.0310	+4.15
		8.3777	..	89.309	33.752	13.728	34.160	49.540	1.80277	+1.652	+0.0297	+3.98
		4.1773	..	138.263	82.706	..	83.706	99.355	1.39161	+1.921	+0.0346	+4.63
		1.6738	..	285.140	229.583	..	232.359	247.950	1.14999	+1.863	+0.0335	+4.48
		0.8326	..	532.791	477.234	..	483.004	498.504	1.06878	+1.772	+0.0319	+4.27
		0.4143	..	1030.159	974.602	..	986.385	1001.820	1.02829	+1.707	+0.0307	+4.11

TABLE III (continued).

Salt.	Temp.	Molal conc.	Wt. of salt.	Wt. of soln.	Wt. of water.	Volume of salt.	Volume of water.	Volume of soln.	Density of soln.	Change in volume, gram of salt.	Change per gram of salt.	Change per mol of salt.
LiI.....	25.00°	8.388	..	89.823	34.266	13.681	34.366	49.504	1.81446	1.457	0.0262	3.50
		4.1802	..	139.284	83.727	..	83.973	99.286	1.40286	1.632	0.0294	3.93
		1.6750	..	287.447	231.890	..	232.571	247.779	1.16009	1.527	0.0275	3.68
		0.8331	..	537.201	481.644	..	483.059	498.156	1.07838	1.416	0.0255	3.41
		0.4146	..	1038.759	983.202	..	986.090	1001.094	1.03762	1.323	0.0238	3.18
		0.1833	..	140.161	84.604	13.633	84.615	99.212	1.41274	0.964	0.0173	2.32
		1.6762	..	288.866	233.309	..	233.340	247.597	1.16668	0.624	0.0112	1.50
		0.8347	..	539.244	483.687	..	483.751	497.866	1.08324	0.422	0.0076	1.02
		0.4149	..	1041.893	986.336	..	986.466	1000.374	1.04150	0.275	0.0050	0.66
		7.6466	50.744	85.361	34.615	12.572	35.405	49.575	1.72186	1.598	0.0315	4.21
	70.19°	3.8131	..	133.939	83.193	..	85.090	99.415	1.34727	1.753	0.0345	4.62
		1.5279	..	279.389	228.643	..	233.858	248.106	1.12609	1.676	0.0330	4.42
		0.7600	..	524.599	473.853	..	484.662	498.816	1.05169	1.582	0.0312	4.17
		0.3782	..	1017.115	966.369	..	988.412	1002.453	1.01463	1.469	0.0289	3.87
		7.6521	..	85.781	35.035	12.539	35.459	49.540	1.73155	1.542	0.0308	4.07
		3.8154	..	134.842	84.096	..	85.113	99.355	1.35717	1.703	0.0336	4.42
		1.5289	..	281.725	230.979	..	233.772	247.950	1.13622	1.639	0.0323	4.32
		0.7604	..	529.362	478.616	..	484.403	498.504	1.06190	1.562	0.0308	4.12
		0.3784	..	1026.750	976.004	..	987.804	1001.817	1.02489	1.474	0.0290	3.89
		7.6576	..	86.300	35.554	12.496	35.659	49.504	1.74329	1.349	0.0266	3.56
	25.00°	3.8181	..	135.852	85.106	..	85.356	99.286	1.36829	1.434	0.0283	3.79
		1.5299	..	284.013	233.267	..	233.952	247.779	1.14624	1.331	0.0262	3.51
		0.7610	..	533.752	483.006	..	484.425	498.156	1.07146	1.235	0.0243	3.25
		0.3787	..	1035.300	984.554	..	987.447	1001.094	1.03417	1.151	0.0227	3.04
		7.6630	..	86.813	36.067	12.452	36.072	49.469	1.75490	0.945	0.0185	2.49
		3.8209	..	136.692	85.946	..	85.957	99.212	1.37778	0.803	0.0158	2.12
		1.5310	..	285.368	234.622	..	234.653	247.597	1.15255	0.492	0.0097	1.30
		0.7615	..	535.727	484.981	..	485.045	497.866	1.07618	0.309	0.0061	0.82
		0.3789	..	1038.358	987.612	..	987.742	1000.374	1.03797	0.180	0.0035	0.47

NaCl....	50.04°	5.1383	14.881	58.287	43.406	6.902	43.932	49.540	1.17656	-1.294	-0.0870	-5.08
		2.5220	..	107.827	92.946	..	94.070	99.353	1.08397	-1.617	-0.1087	-6.36
		1.0266	..	254.912	240.031	..	242.934	247.954	1.02804	-1.882	-0.1265	-7.40
		0.5106	..	502.562	487.681	..	493.578	498.512	1.00812	-1.968	-0.1323	-7.73
		0.2441	..	999.994	985.113	..	997.023	1001.817	0.99818	-2.108	-0.1416	-8.28
25.00°		5.1420	..	58.836	43.955	6.886	44.084	49.504	1.18831	-1.466	-0.0985	-5.76
		2.5638	..	108.842	93.961	..	94.237	99.286	1.09625	-1.837	-0.1235	-7.22
		1.0273	..	257.213	242.332	..	243.045	247.779	1.03807	-2.152	-0.1446	-8.46
		0.5110	..	506.986	492.105	..	493.551	498.163	1.01771	-2.274	-0.1528	-8.94
		0.2343	..	1008.572	993.691	..	996.610	1001.094	1.00747	-2.402	-0.1615	-9.44
0.00°		5.1456	..	59.328	44.447	6.864	44.453	49.469	1.19930	-1.848	-0.1242	-7.26
		2.5957	..	109.613	94.733	..	94.745	99.213	1.10493	-2.396	-0.1610	-9.42
		1.0281	..	258.487	243.606	..	243.638	247.599	1.04397	-2.903	-0.1951	-11.42
		0.5113	..	508.923	494.042	..	494.107	497.823	1.02230	-3.148	-0.2115	-12.36
		0.2345	..	1011.547	996.666	..	996.798	1000.375	1.01117	-3.287	-0.2209	-12.91
NaBr....	70.19°	5.4672	27.895	68.684	40.789	8.755	41.719	49.575	1.38546	-0.899	-0.0322	-3.31
		2.7263	..	117.648	89.753	..	91.800	99.417	1.18338	-1.138	-0.0408	-4.20
		1.0924	..	263.250	235.355	..	240.723	248.104	1.06105	-1.374	-0.0493	-5.07
		0.5433	..	508.498	480.603	..	491.566	498.834	1.01937	-1.487	-0.0533	-5.48
		0.2704	..	1001.013	973.118	..	995.315	1002.453	0.99856	-1.617	-0.0580	-5.97
50.04°		5.4711	..	69.189	41.294	8.734	41.793	49.540	1.39663	-0.987	-0.0354	-3.64
		2.7280	..	118.648	90.753	..	91.850	99.355	1.19418	-1.229	-0.0441	-4.54
		1.0931	..	265.701	237.806	..	240.681	247.954	1.07157	-1.461	-0.0524	-5.39
		0.5437	..	513.379	485.484	..	491.353	498.512	1.02982	-1.575	-0.0565	-5.82
		0.2705	..	1010.769	982.874	..	994.757	1001.817	1.00894	-1.674	-0.0600	-6.18
25.00°		5.4750	..	69.787	41.892	8.709	42.015	49.504	1.40972	-1.220	-0.0438	-4.51
		2.7998	..	119.747	91.852	..	92.122	99.286	1.20608	-1.545	-0.0554	-5.70
		1.0939	..	268.098	240.203	..	240.909	247.779	1.08200	-1.839	-0.0660	-6.79
		0.5441	..	517.899	490.004	..	491.444	498.163	1.03962	-1.990	-0.0714	-7.35
		0.2707	..	1019.448	991.553	..	994.466	1001.094	1.01833	-2.081	-0.0746	-7.68
0.00°		5.4789	..	70.359	42.464	8.682	42.470	49.469	1.42228	-1.683	-0.0603	-6.21

TABLE III (continued).

Salt.	Temp.	Molal concn.	Wt. of salt.	Wt. of soln.	Wt. of water.	Volume of salt.	Volume of water.	Volume of soln.	Density of soln.	Change in volume, gram of salt.	Change per gram of salt.	Change per mol of salt.
NaBr....	0.00°	2.7319	..	120.644	92.749	..	92.761	99.213	1.21601	-2.230	-0.0800	-8.23
		1.0947	..	269.521	241.626	..	241.638	247.599	1.08854	-2.741	-0.0983	-10.11
		0.5444	..	519.945	492.050	..	492.115	497.823	1.04444	-2.974	-0.1066	-10.97
		0.2709	..	1022.601	994.706	..	994.837	1000.374	1.02222	-3.145	-0.1128	-11.61
		0.3425	51.467	1018.482	967.016	14.128	989.074	1002.453	1.01599	-0.749	-0.0146	-2.18
		6.9297	..	86.923	35.456	14.089	35.885	49.540	1.75460	-0.434	-0.0084	-1.26
		1.3553	..	136.307	84.840	..	85.866	99.355	1.37192	-0.600	-0.0117	-1.75
		1.4845	..	283.314	231.847	..	234.650	247.954	1.14261	-0.785	-0.0153	-2.29
		0.6886	..	531.008	479.541	..	485.359	498.512	1.06519	-0.916	-0.0178	-2.67
		0.3427	..	1028.366	976.899	..	988.710	1001.817	1.02650	-0.982	-0.0191	-2.86
NaBr....	25.00°	6.9347	..	87.607	36.140	14.043	36.246	49.504	1.76970	-0.785	-0.0152	-2.28
		3.4577	..	137.580	86.113	..	86.366	99.286	1.38569	-1.123	-0.0218	-3.27
		1.3855	..	285.969	234.502	..	235.191	247.779	1.15413	-1.455	-0.0283	-4.24
		0.6891	..	535.776	484.309	..	485.732	498.163	1.07550	-1.612	-0.0313	-4.69
		0.3429	..	1037.370	985.903	..	988.800	1001.094	1.03624	-1.749	-0.0340	-5.10
		6.9396	..	88.265	36.798	13.997	36.803	49.469	1.78425	-1.331	-0.0258	-3.87
		3.4602	..	138.736	87.269	..	87.281	99.213	1.39837	-2.065	-0.0401	-6.01
		1.3865	..	287.801	236.334	..	236.365	247.599	1.16237	-2.763	-0.0337	-8.05
		0.6896	..	538.328	486.861	..	486.925	497.823	1.08136	-3.099	-0.0602	-9.02
		0.3432	..	1041.056	989.589	..	989.720	1000.375	1.04067	-3.342	-0.0650	-9.74
KCl.....	100.0°	4.101	15.171	56.552	41.381	7.693	43.167	49.617	1.13977	-1.243	-0.0820	-6.11
		2.0448	..	104.678	89.507	..	93.370	99.509	1.05194	-1.554	-0.1024	-7.63
		0.8213	..	247.608	232.437	..	242.468	248.332	0.99938	-1.829	-0.1205	-8.99
		0.2028	..	971.866	956.695	..	997.982	1003.377	0.96860	-2.298	-0.1514	-11.30
		4.5922	16.970	58.256	41.286	8.580	42.228	49.553	1.17539	-1.245	-0.0734	-5.47
		2.2896	..	107.198	90.228	..	92.286	99.406	1.07839	-1.460	-0.0860	-6.41
		0.9174	..	252.891	235.921	..	241.301	248.083	1.01938	-1.799	-0.1060	-7.90
		0.2710	20.250	992.582	972.332	10.239	994.511	1002.348	0.99026	-2.402	-0.1187	-8.84
		2.2910	16.970	108.202	91.232	8.566	92.335	99.348	1.08912	-1.553	-0.0915	-6.82

KCl.....	50.04°	0.9180	..	255.286	238.316	..	241.197	247.943	1.02962	-1.820	-0.1072	-8.00
		0.2711	20.250	1002.343	982.093	10.222	993.957	1001.773	1.00037	-2.406	-0.1188	-8.86
	25.00°	2.2926	16.970	109.138	92.168	8.540	247.439	99.375	1.09935	-1.704	-0.1004	-7.48
		0.9187	..	257.474	240.504	..	241.211	247.745	1.03927	-2.006	-0.1182	-8.81
		0.2713	20.250	1010.864	990.614	10.191	993.326	1001.033	1.00980	-2.664	-0.1316	-9.82
	0.00°	2.2942	16.970	109.789	92.819	8.519	92.831	99.308	1.10664	-2.142	-0.1262	-9.43
		0.9192	..	258.578	241.608	..	241.640	247.602	1.04433	-2.557	-0.1507	-11.22
		0.2715	20.250	1013.792	993.542	10.166	993.671	1000.385	1.01340	-3.452	-0.1705	-12.70
	70.19°	3.3433	12.358	55.702	43.344	6.248	44.333	49.375	1.12359	-1.006	-0.0814	-6.06
		1.6672	..	104.626	92.268	..	94.372	99.415	1.05242	-1.205	-0.0975	-7.26
		0.6680	..	250.155	237.797	..	243.221	248.106	1.00826	-1.363	-0.1103	-8.22
		0.3337	..	493.254	480.896	..	491.865	496.679	0.99310	-1.434	-0.1160	-8.64
		0.1653	..	987.845	975.487	..	997.737	1002.452	0.98543	-1.533	-0.1240	-9.24
	50.04°	3.3457	..	56.151	43.793	6.238	44.323	49.540	1.13345	-1.021	-0.0826	-6.16
		1.6682	..	105.559	93.201	..	94.328	99.355	1.06244	-1.211	-0.0980	-7.30
		0.6685	..	252.538	240.180	..	243.084	247.950	1.01850	-1.372	-0.1110	-8.28
		0.3359	..	498.060	485.702	..	491.574	496.360	1.00343	-1.446	-0.1170	-8.72
		0.1654	..	997.561	985.203	..	997.114	1001.820	0.99575	-1.532	-0.1240	-9.24
	25.00°	3.3481	..	56.628	44.270	6.219	44.400	49.504	1.14391	-1.115	-0.0902	-6.72
		1.6694	..	106.477	94.119	..	94.396	99.286	1.07243	-1.329	-0.1075	-8.02
		0.6689	..	254.710	242.352	..	243.064	247.779	1.02797	-1.504	-0.1216	-9.07
		0.3342	..	502.321	489.963	..	491.402	496.019	1.01271	-1.602	-0.1296	-9.68
		0.1656	..	1006.001	993.643	..	996.562	1001.094	1.00490	-1.687	-0.1365	-10.17
	0.00°	3.3505	..	56.995	44.637	6.204	44.643	49.469	1.15214	-1.378	-0.1123	-8.37
		1.6706	..	107.052	94.694	..	94.706	99.212	1.07902	-1.698	-0.1374	-10.24
		0.6694	..	255.679	243.321	..	243.353	247.597	1.03264	-1.960	-0.1586	-11.82
		0.1657	..	1008.702	996.344	..	996.475	1000.374	1.00832	-2.305	-0.1865	-13.90
	70.19°	4.1696	15.412	57.402	41.990	7.792	42.948	49.375	1.15788	-1.165	-0.0756	-5.64
		2.0792	..	106.397	90.985	..	93.060	99.417	1.07021	-1.435	-0.0932	-6.94
		0.8331	..	251.972	236.560	..	241.954	248.104	1.01559	-1.642	-0.1066	-7.94
		0.4144	..	497.203	481.791	..	492.781	498.834	0.99673	-1.739	-0.1128	-8.41

TABLE III (continued).

Salt.	Temp.	Molal conc.	Wt. of salt.	Wt. of soln.	Wt. of water.	Volume of salt.	Volume of water.	Volume of soln.	Density of soln.	Change in volume.	Change per gram of salt.	Change per mol of salt.
KCl.....	70.19°	0.2062	..	989.660	974.248	..	996.470	1002.453	0.98724	-1.809	-0.1174	-8.75
		4.5983	27.113	67.335	40.222	9.895	40.708	49.540	1.35920	-1.063	-0.0392	-4.66
		2.2928	..	116.753	89.640	..	90.724	99.355	1.17511	-1.264	-0.0466	-5.55
		0.9197	..	263.811	236.698	..	239.560	247.954	1.06395	-1.501	-0.0554	-6.60
KBr.....	50.04°	0.4570	..	511.474	484.361	..	490.217	498.512	1.02600	-1.600	-0.0590	-7.02
		0.2274	..	1008.829	981.716	..	993.585	1001.817	1.00700	-1.663	-0.0613	-7.30
		4.6017	..	67.865	40.752	9.863	40.872	49.504	1.37090	-1.231	-0.0454	-5.40
		2.2944	..	117.778	90.665	..	90.931	99.286	1.18625	-1.508	-0.0556	-6.62
	25.00°	0.9194	..	266.080	238.967	..	239.670	247.779	1.07386	-1.754	-0.0647	-7.70
		0.4573	..	515.866	488.753	..	490.189	498.163	1.03554	-1.889	-0.0696	-8.29
		0.2276	..	1017.381	990.268	..	993.178	1001.094	1.01627	-1.947	-0.0718	-8.55
		2.2961	..	118.510	91.397	9.838	91.409	99.213	1.19450	-2.034	-0.0750	-8.93
	0.00°	0.9200	..	267.289	240.176	..	240.208	247.599	1.07952	-2.447	-0.0902	-10.74
		0.4576	..	517.642	490.529	..	490.594	497.823	1.03981	-2.609	-0.0962	-11.45
		0.2277	..	1020.219	993.106	..	993.237	1000.375	1.01984	-2.700	-0.0996	-11.85
		5.5632	45.755	80.991	35.236	14.693	35.662	49.540	1.63486	-0.815	-0.0178	-2.96
KI.....	50.04°	2.7739	..	130.441	84.686	..	85.710	99.355	1.31288	-1.048	-0.0229	-3.80
		1.1115	..	277.443	231.688	..	234.480	247.954	1.11893	-1.228	-0.0268	-4.46
		0.5529	..	525.125	479.370	..	485.166	498.512	1.05339	-1.347	-0.0294	-4.89
		0.2751	..	1022.473	976.718	..	988.537	1001.817	1.02062	-1.403	-0.0307	-5.09
	25.00°	5.5672	..	81.599	35.844	14.651	35.949	49.504	1.64833	-1.096	-0.0239	-3.98
		2.7758	..	131.370	85.815	..	86.067	99.286	1.32516	-1.432	-0.0313	-5.20
		1.1123	..	279.895	234.140	..	234.828	247.779	1.12962	-1.700	-0.0371	-6.16
		0.5532	..	529.688	483.933	..	485.355	498.163	1.06328	-1.843	-0.0403	-6.65
	0.00°	0.2753	..	1031.233	985.478	..	988.373	1001.094	1.03011	-1.930	-0.0422	-6.97
		5.5712	..	82.143	36.388	14.604	36.393	49.469	1.66049	-1.528	-0.0334	-5.55
		2.7779	..	132.481	86.726	..	86.737	99.213	1.33532	-2.128	-0.0465	-7.72
		1.1131	..	281.389	235.634	..	235.665	247.599	1.13647	-2.670	-0.0584	-9.70
		0.5536	..	531.818	486.063	..	486.127	497.823	1.06829	-2.908	-0.0635	-10.55

KI.....	0.00°	0.2755	..	1034.453	988.698	..	988.829	1000.375	1.03406	-3.058	-0.0668	-11.08
RbCl....	50.04°	6.5223	39.068	75.822	36.754	13.992	37.199	49.540	1.53032	-1.651	-0.0423	5.12
		3.2321	..	125.542	86.474	..	87.520	99.355	1.26337	-2.157	-0.0532	6.68
		1.3031	..	272.785	233.717	..	236.543	247.954	1.10014	-2.581	-0.0661	8.00
		0.6482	..	520.571	481.503	..	487.325	498.512	1.04495	-2.805	-0.0718	8.68
		0.3225	..	1018.037	978.969	..	990.805	1001.817	1.01619	-2.980	-0.0763	9.23
25.00°		6.0890	36.439	74.552	38.113	13.023	38.225	49.495	1.50635	-1.753	-0.0481	5.82
		3.0357	..	124.675	88.236	..	88.496	99.275	1.25585	-2.244	-0.0616	7.44
		1.2165	..	273.163	236.724	..	237.420	247.745	1.10260	-2.698	-0.0740	8.95
		0.6054	..	522.663	486.224	..	487.653	497.774	1.05000	-2.902	-0.0796	9.63
		0.3011	..	1024.613	988.174	..	991.077	1001.053	1.02354	-3.047	-0.0836	10.10
		4.0487	24.229	66.318	42.089	8.659	42.213	49.495	1.33989	-1.377	-0.0568	6.87
		2.0185	..	116.227	91.998	..	92.268	99.275	1.17076	-1.652	-0.0682	8.24
		0.8089	..	264.491	240.262	..	240.968	247.745	1.06759	-1.882	-0.0776	9.39
		0.4026	..	513.860	489.631	..	491.070	497.774	1.03232	-1.955	-0.0806	9.75
		0.2002	..	1015.780	991.551	..	994.464	1001.053	1.01471	-2.070	-0.0854	10.32
		4.9833	29.822	70.108	40.286	10.658	40.404	49.495	1.41647	-1.567	-0.0526	6.36
		2.4845	..	120.113	90.291	..	90.556	99.275	1.20990	-1.939	-0.0650	7.86
		0.9956	..	268.470	238.648	..	239.349	247.745	1.08365	-2.262	-0.0759	9.18
		0.4955	..	517.918	488.096	..	489.530	497.774	1.04047	-2.414	-0.0810	9.80
0.00°		0.2404	..	1019.819	989.997	..	992.906	1001.053	1.01875	-2.511	-0.0842	10.18
		3.2568	39.068	127.256	88.188	13.922	88.200	99.213	1.28265	-2.909	-0.0744	9.01
		1.3050	..	276.347	237.279	..	237.310	247.599	1.11611	-3.633	-0.0930	11.25
		0.6491	..	526.894	487.826	..	487.890	497.823	1.05840	-3.989	-0.1021	12.35
		0.3230	..	1029.616	990.548	..	990.679	1000.375	1.02923	-4.226	-0.1082	13.08
50.04°		5.1739	42.387	80.118	37.731	12.691	38.187	49.540	1.61724	-1.338	-0.0316	5.22
		2.5798	..	129.645	87.258	..	88.313	99.355	1.30487	-1.649	-0.0389	6.43
		1.0337	..	276.713	234.326	..	237.159	247.954	1.11598	-1.896	-0.0448	7.41
		0.5142	..	524.413	482.026	..	487.854	498.512	1.05196	-2.033	-0.0480	7.94
		0.2559	..	1021.814	979.427	..	991.268	1001.817	1.01996	-2.142	-0.0506	8.37
25.00°		5.1777	..	80.658	38.271	12.657	38.383	49.504	1.62932	-1.536	-0.0363	6.00
RbBr....	50.04°											

TABLE III (continued).

Salt.	Temp.	Molal conc.	Wt. of salt.	Wt. of soln.	Wt. of water.	Volume of salt.	Volume of water.	Volume of soln.	Density of soln.	Change in volume.	Change per gram of salt.	Change per mol of salt.
KCl.....	70.19°	0.2052	..	989.660	974.248	..	996.470	1002.453	0.98724	-1.809	-0.1174	-8.75
KBr.....	50.04°	4.5983	27.113	67.335	40.222	9.895	40.708	49.540	1.35920	-1.063	-0.0392	-4.66
		2.2928	..	116.753	89.640	..	90.724	99.355	1.17511	-1.264	-0.0466	-5.55
		0.9197	..	263.811	236.698	..	239.560	247.954	1.06395	-1.501	-0.0554	-6.60
		0.4570	..	511.474	484.361	..	490.217	498.512	1.02600	-1.600	-0.0590	-7.02
	25.00°	0.2274	..	1008.829	981.716	..	993.585	1001.817	1.00700	-1.663	-0.0613	-7.30
		4.6017	..	67.865	40.752	9.863	40.872	49.504	1.37090	-1.231	-0.0454	-5.40
		2.2944	..	117.778	90.665	..	90.931	99.286	1.18625	-1.508	-0.0536	-6.62
		0.9194	..	266.080	238.967	..	239.670	247.779	1.07386	-1.754	-0.0647	-7.70
		0.4573	..	515.866	488.753	..	490.189	498.163	1.03534	-1.889	-0.0696	-8.29
	0.00°	0.2276	..	1017.381	990.268	..	993.178	1001.094	1.01627	-1.947	-0.0718	-8.55
		2.2961	..	118.510	91.397	9.838	91.409	99.213	1.19450	-2.034	-0.0750	-8.93
		0.9200	..	267.289	240.176	..	240.208	247.599	1.07952	-2.447	-0.0902	-10.74
		0.4576	..	517.642	490.529	..	490.594	497.823	1.03981	-2.609	-0.0962	-11.45
		0.2277	..	1020.219	993.106	..	993.237	1000.375	1.01984	-2.700	-0.0996	-11.85
KI.....	50.04°	5.5632	45.755	80.991	35.236	14.693	35.662	49.540	1.63486	-0.815	-0.0178	-2.96
		2.7739	..	130.441	84.686	..	85.710	99.355	1.31288	-1.048	-0.0229	-3.80
		1.1115	..	277.443	231.688	..	234.480	247.954	1.11893	-1.228	-0.0268	-4.46
		0.5559	..	525.125	479.370	..	485.166	498.512	1.05339	-1.347	-0.0294	-4.89
	25.00°	0.2731	..	1022.473	976.718	..	988.527	1001.817	1.02062	-1.403	-0.0307	-5.09
		5.5672	..	81.599	35.844	14.651	35.949	49.504	1.64833	-1.096	-0.0239	-3.98
		2.7758	..	131.570	85.815	..	86.067	99.286	1.32516	-1.432	-0.0313	-5.20
		1.1123	..	279.895	234.140	..	234.828	247.779	1.12962	-1.700	-0.0371	-6.16
		0.5532	..	529.688	483.933	..	485.355	498.163	1.06328	-1.843	-0.0403	-6.65
	0.00°	0.2753	..	1031.233	985.478	..	988.373	1001.094	1.03011	-1.930	-0.0422	-6.97
		5.5712	..	82.143	36.388	14.604	36.393	49.469	1.66049	-1.528	-0.0334	-5.55
		2.7779	..	132.481	86.726	..	86.737	99.213	1.33532	-2.128	-0.0465	-7.72
		1.1131	..	281.389	235.634	..	235.665	247.599	1.13647	-2.670	-0.0584	-9.70
		0.5536	..	531.818	486.063	..	486.127	497.823	1.06829	-2.908	-0.0635	-10.55

KI.....	0.00°	1034.453	988.698	..	988.829	1000.375	1.03406	-3.058	-0.0668	-11.08
RbCl.....	50.04°	75.822	36.734	13.992	37.199	49.540	1.53032	-1.651	-0.0423	-5.12
		125.542	86.474	..	87.520	99.355	1.26357	-2.157	-0.0532	-6.68
		272.785	233.717	..	236.543	247.954	1.10014	-2.581	-0.0661	-8.00
		520.571	481.503	..	487.325	498.512	1.04495	-2.805	-0.0718	-8.68
		1018.037	978.969	..	990.805	1001.817	1.01619	-2.980	-0.0763	-9.23
	25.00°	74.552	38.113	13.023	38.225	49.495	1.50625	-1.753	-0.0481	-5.82
		124.675	88.236	..	88.496	99.275	1.25585	-2.244	-0.0616	-7.44
		273.163	236.724	..	237.420	247.745	1.10260	-2.698	-0.0740	-8.95
		522.663	486.224	..	487.653	497.774	1.05000	-2.902	-0.0796	-9.63
		1024.613	988.174	..	991.077	1001.053	1.02354	-3.047	-0.0836	-10.10
		66.318	42.089	8.659	42.213	49.495	1.33989	-1.377	-0.0568	-6.87
		116.227	91.998	..	92.268	99.275	1.17076	-1.652	-0.0682	-8.24
		264.491	240.262	..	240.968	247.745	1.06759	-1.882	-0.0776	-9.39
		513.860	489.631	..	491.070	497.774	1.03232	-1.955	-0.0806	-9.75
		1015.780	991.551	..	994.464	1001.053	1.01471	-2.070	-0.0854	-10.32
		70.108	40.286	10.658	40.404	49.495	1.41647	-1.567	-0.0526	-6.36
		120.113	90.591	..	90.556	99.275	1.20990	-1.939	-0.0650	-7.86
		268.470	238.648	..	239.349	247.745	1.08365	-2.262	-0.0759	-9.18
		517.918	488.096	..	489.530	497.774	1.04047	-2.414	-0.0810	-9.80
		1019.819	989.997	..	992.906	1001.053	1.01875	-2.511	-0.0842	-10.18
	0.00°	127.256	88.188	13.922	88.200	99.213	1.28265	-2.909	-0.0744	-9.01
		276.347	237.279	..	237.310	247.599	1.11611	-3.633	-0.0930	-11.25
		526.894	487.826	..	487.890	497.823	1.05840	-3.989	-0.1021	-12.35
		1029.616	990.548	..	990.679	1000.375	1.02923	-4.226	-0.1082	-13.08
		80.118	37.731	12.691	38.187	49.540	1.61724	-1.338	-0.0316	-5.22
	50.04°	129.645	87.258	..	88.313	99.355	1.30487	-1.649	-0.0389	-6.43
		276.713	234.326	..	237.159	247.954	1.11598	-1.896	-0.0448	-7.41
		524.413	482.026	..	487.854	498.512	1.05196	-2.033	-0.0480	-7.94
		1021.814	979.427	..	991.268	1001.817	1.01996	-2.142	-0.0506	-8.37
	25.00°	80.658	38.271	12.657	38.383	49.504	1.62932	-1.536	-0.0363	-6.00
RbBr.....	50.04°	5.1739	42.387
		2.5798
		1.0337
		0.5142
		0.2559
	25.00°	5.1777

TABLE III (continued).

Salt.	Temp.	Molal conc.	Wt. of salt.	Wt. of soln.	Wt. of water.	Volume of salt.	Volume of water.	Volume of soln.	Density of soln.	Change in volume, gram of salt.	Change per mol of salt.
RbBr.....	25.00°	2.5816	..	130.653	88.266	..	88.525	99.286	1.31593	-1.896	-0.0448
		1.0345	..	279.020	236.633	..	237.328	247.779	1.12608	-2.206	-0.0321
		0.5145	..	528.829	486.442	..	487.871	498.163	1.06156	-2.365	-0.0358
		0.2560	..	1030.376	987.989	..	990.893	1001.094	1.02925	-2.456	-0.0380
		2.5835	..	131.424	89.037	12.623	89.049	99.213	1.32467	-2.459	-0.0380
	0.00°	1.0352	..	280.287	237.900	..	237.931	247.599	1.13202	-2.955	-0.0698
		0.5149	..	530.704	488.317	..	488.382	497.823	1.06605	-3.182	-0.0751
		0.2562	..	1033.359	990.972	..	991.103	1000.375	1.03297	-3.351	-0.0791
		5.5699	58.600	92.362	33.762	16.540	34.170	49.540	1.86439	-1.170	-0.0200
		2.7772	..	141.839	83.239	..	84.245	99.355	1.42760	-1.430	-0.0244
RbI.....	25.00°	1.1129	..	288.857	230.257	..	233.041	247.954	1.16496	-1.627	-0.0278
		0.5535	..	536.534	477.934	..	483.712	498.512	1.07627	-1.740	-0.0297
		0.2754	..	1033.889	975.289	..	987.080	1001.817	1.03201	-1.803	-0.0308
		2.7792	..	142.964	84.364	16.502	84.612	99.286	1.43992	-1.828	-0.0312
		1.1136	..	291.323	232.723	..	233.407	247.779	1.17574	-2.130	-0.0364
	0.00°	0.5539	..	541.107	482.507	..	483.924	498.163	1.08620	-2.265	-0.0387
		0.2756	..	1042.641	984.041	..	986.932	1001.094	1.04150	-2.340	-0.0399
		2.7813	..	143.868	85.268	16.461	85.279	99.213	1.45009	-2.527	-0.0431
		1.1144	..	292.804	234.204	..	234.236	247.599	1.18257	-3.098	-0.0329
		0.5543	..	543.245	484.645	..	484.709	497.823	1.09124	-3.347	-0.0371
CsCl.....	70.19°	0.2758	..	1045.934	987.334	..	987.464	1000.375	1.04554	-3.350	-0.0606
		7.5180	62.715	94.409	31.694	15.869	32.416	49.575	1.90437	+1.290	+0.0206
		4.2990	35.862	75.010	39.148	9.074	40.041	49.575	1.51306	+0.460	+0.0128
		2.1437	..	124.010	88.148	..	90.138	99.417	1.24737	+0.185	+0.0052
		0.8590	..	269.603	233.741	..	239.071	248.104	1.08665	-0.041	-0.0011
	50.04°	0.4272	..	514.879	479.017	..	489.942	498.834	1.03214	-0.182	-0.0051
		0.2126	..	1007.337	971.475	..	993.628	1002.453	1.00487	-0.249	-0.0069
		7.5233	62.715	94.820	32.105	15.833	32.494	49.540	1.91401	+1.213	+0.0193
		4.3020	35.862	75.447	39.585	9.054	40.065	49.540	1.52295	+0.421	+0.0117

CsCl.....	50.04°	2.1451	..	124.921	89.039	..	90.136	99.353	1.25732	+0.165	+0.0046	+0.78
		0.8596	..	271.969	236.107	..	238.961	247.954	1.09685	-0.061	-0.0017	-0.29
		0.4275	..	519.648	483.786	..	489.637	498.512	1.04240	-0.179	-0.0050	-0.84
		0.2127	..	1017.005	981.143	..	993.009	1001.817	1.01516	-0.246	-0.0069	-1.15
		25.00°	7.5288	62.715	95.322	32.607	15.782	49.504	1.92554	+1.019	+0.0162	+2.75
		4.3051	35.862	75.939	40.077	9.024	40.195	49.504	1.53400	+0.285	+0.0079	+1.34
		2.1465	..	125.864	90.002	..	90.266	99.286	1.26769	-0.004	-0.0001	-0.02
		0.8601	..	274.178	238.316	..	239.017	247.779	1.10654	-0.262	-0.0073	-1.23
		0.4278	..	523.938	488.076	..	489.510	498.163	1.05174	-0.371	-0.0103	-1.74
		0.2129	..	1025.487	989.625	..	992.532	1001.094	1.02437	-0.462	-0.0129	-2.17
		0.00°	4.3082	..	76.364	40.502	8.992	49.469	1.54367	-0.090	-0.0008	-0.14
		2.1481	..	126.519	90.657	..	90.669	99.213	1.27523	-0.448	-0.0135	-2.10
CsBr.....	70.19°	0.8608	..	275.272	239.410	..	239.442	247.599	1.11177	-0.835	-0.0233	-3.92
		0.4281	..	525.604	489.742	..	489.807	497.823	1.08581	-0.976	-0.0272	-4.58
		0.2130	..	1028.223	992.361	..	992.492	1000.375	1.02784	-1.109	-0.0310	-5.21
		4.1801	44.084	82.094	38.010	10.006	38.877	49.575	1.65596	+0.692	+0.0157	+3.34
		3.0665	32.340	73.206	40.866	7.340	41.798	49.575	1.47667	+0.437	+0.0135	+2.85
		1.5292	..	122.071	89.731	..	91.780	99.417	1.22787	+0.297	+0.0092	+1.95
		0.6127	..	267.552	235.212	..	240.576	248.104	1.07839	+0.188	+0.0058	+1.24
		0.3048	..	512.742	480.402	..	491.357	498.834	1.02788	+0.137	+0.0042	+0.90
		0.1517	..	1005.211	972.871	..	995.056	1002.453	1.00275	+0.037	+0.0018	+0.36
		50.04°	4.1831	44.084	82.559	38.474	38.940	49.540	1.66651	+0.622	+0.0141	+3.00
		3.0687	32.340	73.676	41.336	7.320	41.837	49.540	1.48720	+0.383	+0.0118	+2.52
		1.5301	..	123.024	90.684	..	91.782	99.355	1.23823	+0.253	+0.0078	+1.66
	25.00°	0.6131	..	269.953	237.613	..	240.487	247.954	1.08872	+0.147	+0.0045	+0.96
		0.3050	..	517.592	485.252	..	491.121	498.512	1.03827	+0.071	+0.0022	+0.47
		0.1518	..	1014.970	982.630	..	994.514	1001.897	1.01313	-0.017	-0.0005	-0.01
		4.1861	44.084	83.094	39.010	9.945	39.125	49.504	1.67853	+0.434	+0.0099	+2.09
		3.0709	32.340	74.192	41.852	7.295	41.975	49.504	1.49871	+0.234	+0.0072	+1.54
		1.5312	..	123.981	91.641	..	91.910	99.286	1.24873	+0.081	+0.0025	+0.53
		0.6136	..	272.163	239.823	..	240.528	247.779	1.09841	-0.044	-0.0014	-0.29

TABLE III (continued).

Salt.	Temp.	Molal conc.	Wt. of salt.	Wt. of soln.	Wt. of water.	Volume of salt.	Volume of water.	Volume of soln.	Density of soln.	Change in volume.	Change per gram of salt.	Change per mol of salt.
CsBr.....	25.00°	0.3052	..	521.898	489.558	..	490.996	498.163	1.04765	-0.126	-0.0040	-0.84
		0.1519	..	1023.423	991.083	..	993.995	1001.094	1.02230	-0.198	-0.0061	-1.29
		3.0731	..	74.608	42.268	7.269	42.274	49.469	1.50818	-0.074	-0.0023	-0.49
		1.5323	..	124.596	92.256	..	92.268	99.213	1.25584	-0.324	-0.0100	-2.13
		0.6140	..	273.169	240.829	..	240.861	247.599	1.10327	-0.531	-0.0164	-3.49
	0.00°	0.3054	..	523.466	491.126	..	491.191	497.823	1.05151	-0.637	-0.0197	-4.19
		0.1520	..	1026.026	993.686	..	993.817	1000.375	1.02564	-0.711	-0.0220	-4.67
		2.8931	37.252	76.883	39.631	8.315	40.534	49.575	1.55084	+0.726	+0.0195	+5.06
		1.4427	..	125.694	88.442	..	90.459	99.417	1.26431	+0.643	+0.0173	+4.48
		0.5781	..	271.120	233.868	..	239.201	248.104	1.09277	+0.588	+0.0158	+4.10
CsI.....	50.04°	0.2875	..	516.330	479.078	..	490.003	498.834	1.03507	+0.516	+0.0138	+3.60
		0.1431	..	1008.692	971.440	..	993.593	1002.453	1.00622	+0.545	+0.0146	+3.80
		2.8952	..	77.386	40.134	8.291	40.620	49.540	1.56209	+0.629	+0.0169	+4.39
		1.4436	..	126.695	89.443	..	90.525	99.355	1.27517	+0.539	+0.0145	+3.76
		0.5784	..	273.574	236.322	..	239.180	247.954	1.10333	+0.483	+0.0130	+3.37
	25.00°	0.2877	..	521.209	483.957	..	489.810	498.512	1.04553	+0.411	+0.0110	+2.86
		0.1432	..	1018.539	981.287	..	993.155	1001.817	1.01669	+0.371	+0.0100	+2.59
		2.8973	..	77.989	40.737	8.262	40.857	49.504	1.57541	+0.385	+0.0103	+2.68
		1.4446	..	127.712	90.460	..	90.726	99.286	1.28630	+0.298	+0.0080	+2.08
		0.5789	..	275.858	238.606	..	239.307	247.779	1.11332	+0.210	+0.0056	+1.46
CsI.....	0.00°	0.2879	..	525.588	488.336	..	489.771	498.163	1.05505	+0.130	+0.0035	+0.91
		0.1433	..	1027.064	989.812	..	992.720	1001.094	1.02594	+0.112	+0.0030	+0.78
		1.4456	..	128.392	91.140	8.232	91.152	99.213	1.29411	-0.171	-0.0046	-1.19
		0.5793	..	276.940	239.688	..	239.720	247.599	1.11850	-0.353	-0.0095	-2.46
		0.2881	..	527.224	489.972	..	490.037	497.823	1.05906	-0.446	-0.0120	-3.11
		0.1434	..	1029.748	992.496	..	992.627	1000.375	1.02936	-0.484	-0.0130	-3.37

Sodium and potassium chlorides produce the greatest contraction during solution, between 0.1 and 0.2 cc. per gram of salt except at the highest temperatures and concentrations.

With the other salts the contractions both per gram and per gram molecule vary irregularly between fairly narrow limits, at 25° between 0.02 and 0.09 cc. per gram of salt.

In the case of salts of the same metal with different halogens, the contraction is always greatest with chlorides and least with iodides. The only exception to this rule noted in the earlier paper, sodium bromide, has disappeared owing to the use of the new value of the density of the solid salt.

In general, contraction increases and expansion diminishes with increasing dilution. This increase in contraction with increasing dilution is greatest with chlorides and least with iodides. It is also noticeable that the rate of increase is greatest with lithium chloride, and much less for rubidium and caesium chlorides than for the corresponding salts of sodium and potassium. Bromides of the different metals show no marked differences in the rate of increase, and the same is true of the iodides.

Lithium iodide and lithium bromide in very concentrated solutions at 25° and above, show increasing expansion with increasing dilution.

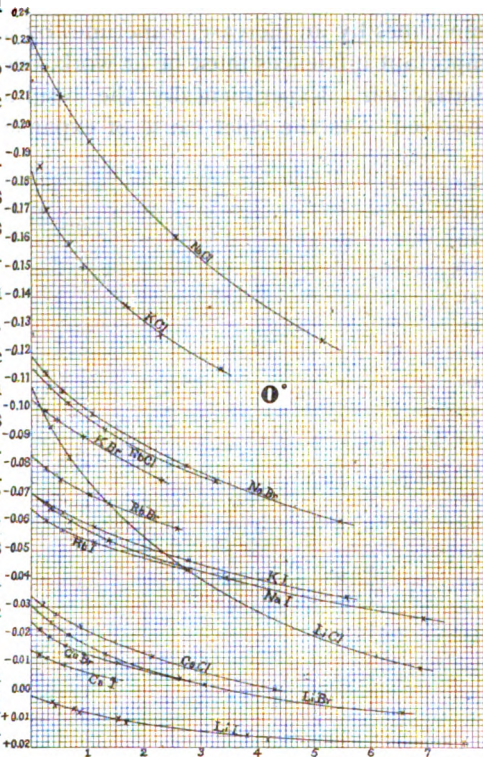


Fig. 1.

All the curves seem to approach the horizontal axis with increasing concentration, *i. e.*, in most cases the greater the change in volume, the steeper the curve. With unlimited solubility necessarily a zero value for change in volume would eventually be reached, when the water disappeared from the solution. But this point is far beyond the practical limits of solubility even with the most soluble salts.

From 0° to 50° all the salts examined except lithium chloride and up to 70° most of the salts at a given concentration show diminishing contraction or increasing expansion with rising temperature. In the case of both lithium chloride and bromide, however, the contraction is greater at 70°

than at 50° and with lithium chloride it is least at 25° and even greater at 100° than at 0° . Potassium chloride also shows greater contraction at 100° than at 25° .

In the earlier paper a suggestion was advanced as to the causes of these varied changes in volume during solution, based upon the hypothesis of compressible atoms previously proposed by T. W. Richards. While the earlier paper should be consulted for details, the main features of the explanation are summed up below.

It was pointed out that, since the solution of salts in water is accompanied sometimes by an increase, sometimes by a decrease in volume, *at least two* important influences must be at work, one producing expansion, the other contraction. Experimentally the resultant of the combined effects is observed. As the chief cause of expansion, it was suggested that, since

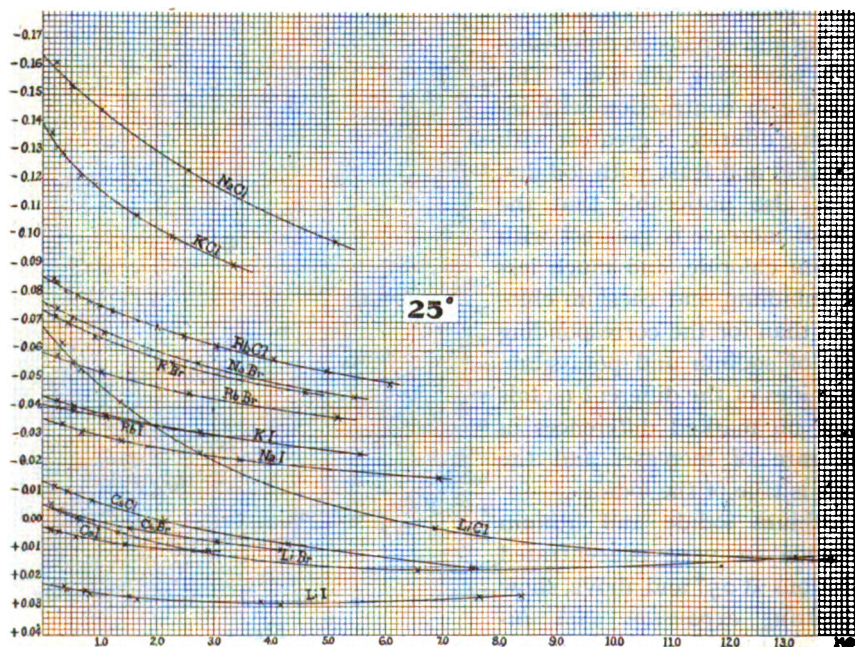


Fig. 2.

the *formation* of the solid salts in question from the solid or liquid elements is accompanied by a very marked contraction, from 15% with lithium iodide to 56% with caesium chloride,¹ the *dissociation* of the salts during solution should tend to produce a corresponding expansion.²

¹ See Table V on page 96.

² In a paper published nearly a year later than the first one of this series, Heydweiller suggests dissociation as a cause for expansion during solution but without giving any idea of the magnitude of the effect to be expected. *Ann. Physik*, 37, 762 (1912).

As the chief cause of contraction was proposed the combination of the ions and the molecules with water, *i. e.*, ionic or molecular hydration.¹

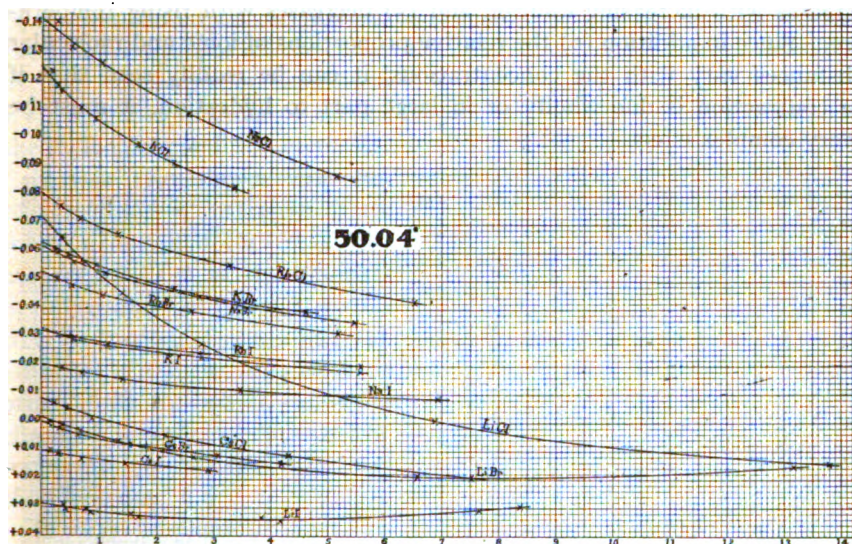


Fig. 3.

The magnitude of this effect may be expected to vary with (1) the extent of the hydration, *i. e.*, the quantities of material concerned, (2) the magnitude of the affinities involved, (3) the compressibilities of the metals and

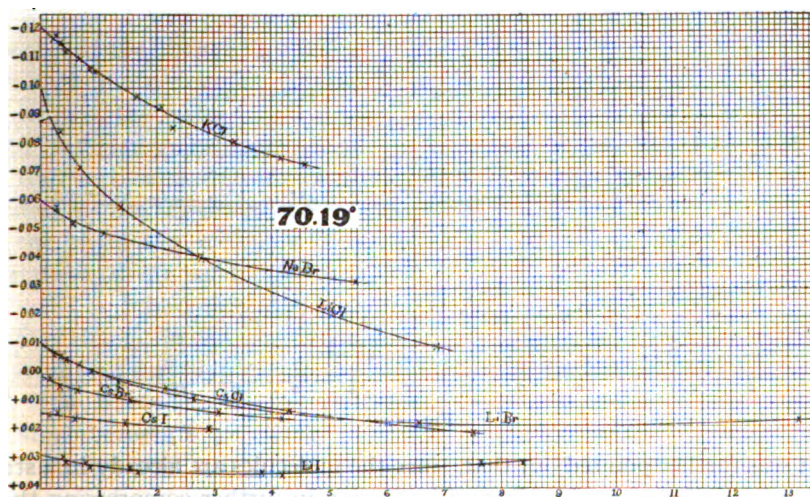


Fig. 4.

¹ The idea of compression of the hydrated substance and the water by chemical combination was first proposed by Richards (*Proc. Amer. Acad.*, 37, 13 (1901)).

halogens, and of the water. Furthermore the extent of the hydration is undoubtedly not constant for any one ionic or molecular species, but (4) increases with increasing dilution and (5) decreases with rising temperature. Since in addition (6) the relative proportions of ionic and molecular substances vary with the concentrations, it can be readily seen that if the contraction is due wholly or in large part to hydration, it must be a very complex effect.

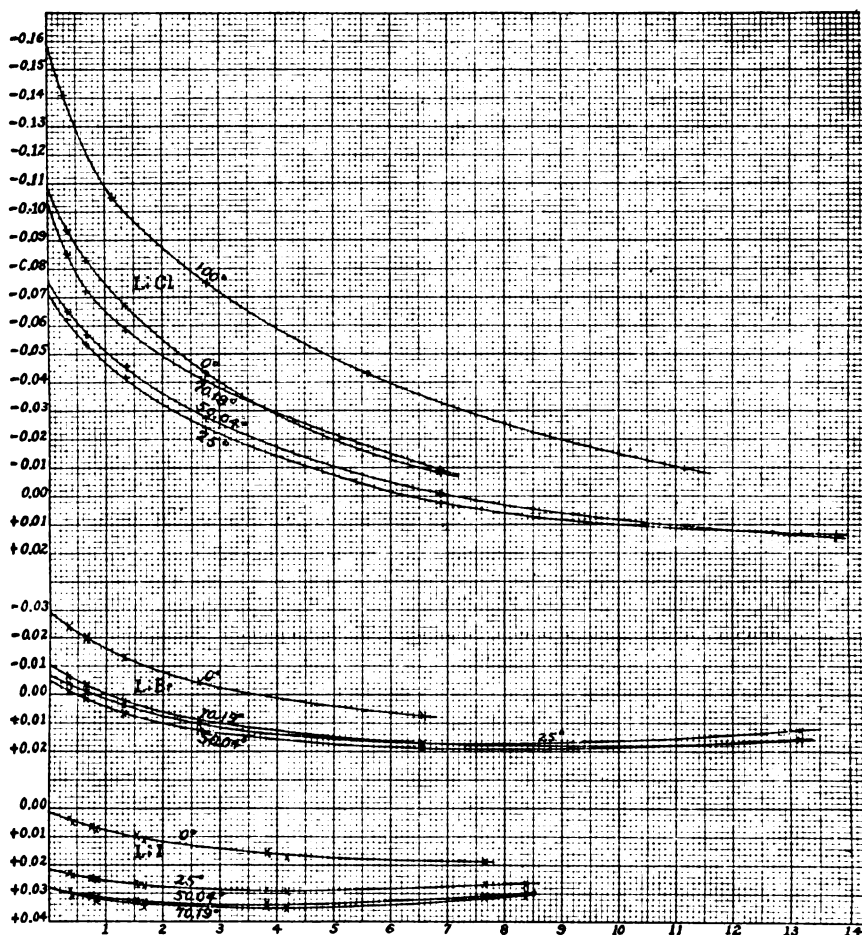


Fig. 5.

It was further pointed out that, since the molecules are already in a state of great compression, the effect of hydration in further compressing them must be small. For this reason, if for no other, the resultant change in volume during solution produced by the molecules should at any rate be less than that produced by the ions. Furthermore, judging from the fact

that few of the salts in question form solid hydrates at ordinary temperatures and that even these hydrates are not particularly stable, the molecular hydration cannot be very extensive in most cases. This is in accord with the general trend of all the curves toward low values for change in volume as the concentration increases, *i. e.*, as the proportion of salt in the molecular condition increases.

It was also shown that the effects observed in fairly dilute solution are in accord with the compressibilities of the elements involved and the water, the relative hydration of the ions,¹ the affinities of the elements for each other and for water, and the change in volume during the formation of the solid salt from the elements.

It was emphasized that although the varying polymerization of water undoubtedly plays some part in the change, it certainly is not the determining factor, since the observed effects are not in accord with those to be expected if the change in volume is due wholly to changing polymerization of the water.

An interesting comparison of the different salts was obtained by finding the algebraic sum of (a) the change in volume in the formation of the solid salt from the solid or liquid elements, and

(b) the change in volume during solution. This sum, which is negative for all fifteen salts, represents the contraction in the formation of the solution from water and the free elements. Obviously, in very dilute solution the sum represents the change in volume in the formation of ions from the free elements and water, while in more concentrated solutions it refers to both ionized and un-ionized substances in varying proportions.

¹ Washburn and Millard have recently found the caesium ion to be more highly hydrated than the chloride ion, although less hydrated than the potassium ion. *THIS JOURNAL*, 37, 694 (1915).

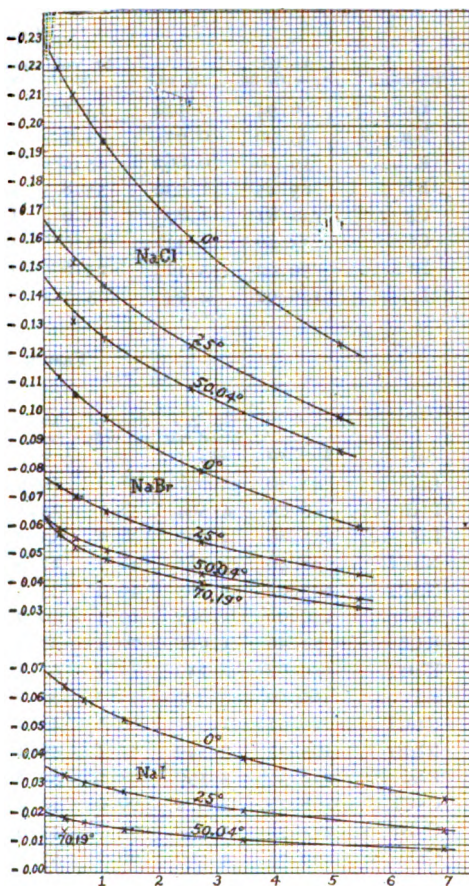


Fig. 6.

Owing to the availability of new data, the following tables, which give the values of the sum $a + b$, together with the data from which the computations are made, are reprinted from the earlier paper with the necessary corrections.

TABLE IV.

Element.	At. wt. Ag=107.88.	Sp. gr. ¹	At. vol. cc.	Compressi- bility ² megabars × 10 ⁶ .	Heat of oxidation. Kilogram calories.	Heat of combina- tion with hydro- gen. ⁴ Kilo- gram calories.
Li.....	6.94	0.534	13.1	9.0	143(2M + O) ³	..
Na.....	23.00	0.971	23.7	15.6	101(2M + O) ³	..
K.....	39.10	0.862	45.4	31.7	87(2M + O) ³	..
Rb.....	85.45	1.532	55.8	40.0	84(2M + O) ³	..
Cs.....	132.81	1.87	71.0	61.0	83(2M + O) ³	..
Cl.....	35.46	1.412	25.0	95.0	-18(Cl ₂ O)	22.0
Br.....	79.92	3.121	25.6	52.0	...	8.4
I.....	126.92	4.94	25.7	13.0	45(I ₂ O ₅)	-6.0

TABLE V.

Salt.	Mol. wt.	Sp. gr. ¹ fused salt at 25°.	Sum of at. vols. cc.	Mol. vol. cc.	Contraction in formation of solid = a. cc.	Change in vol. ² during soln. at 25° = b. cc.	a + b. cc.	Compressi- bility ⁷ megabars × 10 ⁶ .
LiCl.....	42.40	2.068	38.1	20.5	-17.6	-2.03	-19.6	...
LiBr.....	86.86	4.364	38.7	25.1	-13.6	+0.16	-13.4	...
LiI.....	133.86	4.061	38.8	33.0	-5.8	+3.40	-2.4	...
NaCl....	58.46	2.162	48.7	27.0	-21.7	-8.48	-30.2	4.1
NaBr....	102.92	3.203	49.3	33.1	-17.2	-6.94	-24.1	5.1
NaI.....	149.92	3.665	49.4	40.9	-8.5	-4.50	-13.0	6.9
KCl.....	74.56	1.988	70.4	37.5	-32.9	-8.71	-41.6	5.0
KBr.....	119.02	2.749	71.0	43.3	-27.7	-7.72	-35.4	6.2
KI.....	166.02	3.123	71.1	53.2	-17.9	-6.31	-24.2	8.6
RbCl....	120.91	2.798	80.8	43.2	-37.6	-9.19	-46.8	...
RbBr....	165.37	3.349	81.4	49.4	-32.0	-8.70	-40.7	...
RbI.....	212.37	3.550	81.5	59.8	-21.7	-7.86	-29.6	...
CsCl....	168.27	3.974	96.0	42.4	-53.6	-1.09	-54.7	...
CsBr....	212.73	4.433	96.6	47.9	-48.7	0.00	-48.7	...
CsI.....	259.73	4.509	96.7	57.6	-39.1	+1.77	-37.3	...

¹ For the specific gravities of the alkali metals see Richards and Brink, *THIS JOURNAL*, 29, 117 (1907).

² Richards, Stull and Bonnet, *Pub. Carnegie Inst.*, 76, 15 (1907); Richards and Stull, *Ibid.*, 7 (1903); Richards, *THIS JOURNAL*, 37, 1643 (1915).

³ Abegg, "Handb. d. anorg. Chem.," Vol. II, Part I.

⁴ Landolt-Börnstein-Roth, "Tabellen," 1912.

⁵ For the specific gravities of the salts of sodium, potassium rubidium, and caesium, see a subsequent paper to appear in the February number of *THIS JOURNAL*; for those of the lithium salts, see Baxter, *Am. Chem. J.*, 31, 559 (1904).

⁶ The values refer to molal solutions and are obtained by multiplying values taken from the curves on page 92 by the molecular weights.

⁷ Richards and Jones, *THIS JOURNAL*, 31, 158 (1909). If the most recent value of the compressibility of mercury is used these values become slightly larger.

The sum $a + b$, which represents, in cubic centimeters, the contraction produced in the formation of the solution from one gram atom each of the free metal and halogen and the water, was previously found to be additive for lithium, sodium, and potassium salts at 1 molal concentration and below. Values are given in Table VI for all fifteen salts at various concentrations up to five molal, at 25°, which show not only that the property is additive for the rubidium and cesium salts as well, but also that the additive relationship holds for all fifteen salts at high concentrations.

In connection with these tables it is interesting to note that since the values are obtained from the expression (Atomic Volume of Metal + Atomic Volume of Halogen — Molecular Volume of Salt) + (Molecular Volume of Salt + Volume of Water — Volume of Solution), they are independent of the molecular volumes (and hence the specific gravities) of the solid salts, and that while the absolute values are dependent on both the atomic volumes of the free elements and the observed change in volume during solution, the additive relationships depend upon the latter alone.

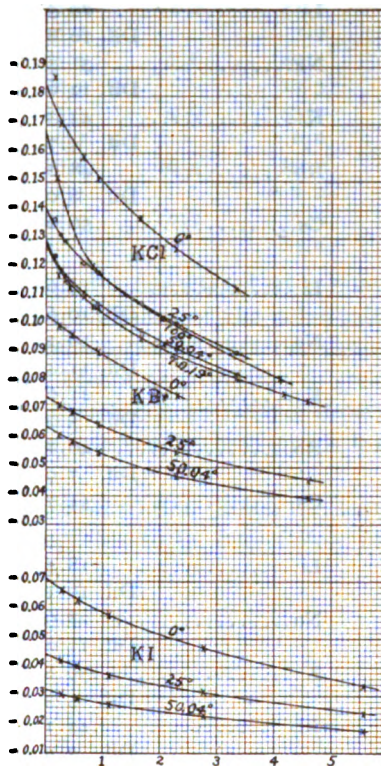


Fig. 7.

It is not surprising to find the additive relationships holding closely at the lower concentrations, where the greater portion of the salt is in the ionic state, but that these relationships should hold so closely at concentrations as high as 5 molal is curious, to say the least. The fact that the curves representing change in volume at different concentrations are far from parallel makes the relationship all the more striking. The obvious significance of this feature is that the change in volume which takes place when the free elements become dissolved *molecules* of salt also is an additive property.

It is difficult to believe that this coincidence is a chance one. The cause may be sought first in the probability, previously emphasized, that the change in volume produced by the undissociated molecules at high concentrations at any rate is small, and second in the fact that the molecular volumes of the solid salts themselves are not far from additive, as Table VII shows.

TABLE VI.
Infinite Dilution.

	Cl.	Dif.	Br.	Dif.	I.
Li.....	20.5	6.4	14.1	11.3	2.8
	Dif. 10.8		11.0		11.1
Na.....	31.3	6.2	25.1	11.2	13.9
	Dif. 12.0		11.4		11.3
K.....	43.3	6.8	36.5	11.3	25.2
	Dif. 4.7		5.3		5.2
Rb.....	48.0	6.2	41.8	11.4	30.4
	Dif. 8.0		8.2		8.2
Cs.....	56.0	6.0	50.0	11.4	38.6
1 Molal. ¹					
Li.....	19.6	6.2	13.4	11.0	2.4
	Dif. 10.6		10.7		10.6
Na.....	30.2	6.1	24.1	11.1	13.0
	Dif. 11.4		11.3		11.2
K.....	41.6	6.2	35.4	11.2	24.2
	Dif. 5.2		5.3		5.4
Rb.....	46.8	6.1	40.7	11.1	29.6
	Dif. 7.9		8.0		7.7
Cs.....	54.7	6.0	48.7	11.4	37.3
3 Molal.					
Li.....	18.5	6.0	12.5	10.5	2.0
	Dif. 10.1		10.2		10.0
Na.....	28.6	5.9	22.7	10.7	12.0
	Dif. 11.2		11.1		11.0
K.....	39.8	6.0	33.8	10.8	23.0
	Dif. 5.3		5.3		5.2
Rb.....	45.1	6.0	39.1	10.9	28.2
	Dif. 7.9		8.0		8.2
Cs.....	53.0	5.9	47.1	10.7	36.4
5 Molal.					
Li.....	17.9	5.7	12.2	10.2	2.0
	Dif. 9.6		9.7		9.3
Na.....	27.5	5.6	21.9	10.6	11.3
			Dif. 11.0		10.8
K.....	Dif. 16.5		32.9	10.8	22.1
			Dif. 5.2		
Rb.....	44.0	5.9	38.1		
	Dif. 7.9		8.0		
Cs.....	51.9	5.8	46.1		

When one considers the large variation in the contraction which takes place in the formation of the solid salts from the elements, from 15% with lithium iodide to 56% with caesium chloride, even this rough additive relationship is noteworthy.

¹ Similar data for barium chloride and bromide obtained by Mr. P. B. Goode give values 57.7 and 44.7, respectively, with a difference of 2 (6.5). This value is not far from the average difference between chlorides and bromides of the univalent elements.

TABLE VII.
Molecular Volumes of Solid Salts.

	Cl.	DM.	Br.	DM.	I.
Li.....	20.5	4.6	25.1	7.9	33.0
	Dif. 6.5		8.0		7.9
Na.....	27.0	6.1	33.1	7.8	40.9
	Dif. 10.5		10.2		12.3
K.....	37.5	5.8	43.3	9.9	53.2
	Dif. 5.7		6.1		6.6
Rb.....	43.2	6.2	49.4	10.4	59.8
	Dif. —0.8		—1.5		—2.2
Cs.....	42.4	5.5	47.9	9.7	57.6
Cs-Li.....	21.9		22.8		24.6

Since the salts are undoubtedly not all equally dissociated at a given molal concentration, and since the molecular volumes of the solid salts are only approximately additive, it is not to be expected that the values for the sum ($a + b$) will be strictly additive, except at a dilution so great that dissociation is nearly complete. But at such concentrations experimental values for change in volume during solution become much less accurate.

At 0° , 50° and 70° , and within the same concentration limits, the same additive relationships hold. Figures showing this to be true follow for as many instances as it seems worth while to give.

 TABLE VIII.
Infinite Dilution, 0° .

	Cl.	Dif.	Br.	Dif.	I.
Li.....	22.2	5.9	16.3	10.8	5.5
	Dif. 13.1		13.1		13.5
Na.....	35.3	5.9	29.4	10.4	19.0
	Dif. 11.3		10.6		10.5
K.....	46.6	6.6	40.0	10.5	29.5
	Dif. 4.9		5.8		5.9
Rb.....	51.5	5.7	45.8	10.4	35.4
	Dif. 7.8		8.1		7.5
Cs.....	59.3	5.4	53.9	11.0	42.9
1 Molal, 0° .					
Li.....	20.8	5.8	15.0	10.2	4.8
	Dif. 12.4		12.5		12.3
Na.....	33.2	5.7	27.5	10.4	17.1
	Dif. 10.9		10.8		10.6
K.....	44.1	5.8	38.3	10.6	27.7
	Dif. 5.2		5.3		5.4
Rb.....	49.3	5.7	43.6	10.5	33.1
	Dif. 7.9		7.9		7.7
Cs.....	57.2	5.7	51.5	10.7	40.8
3 Molal, 0° .					
Li.....	19.3	5.5	13.8	9.9	3.9
	Dif. 11.4		11.4		11.0

TABLE VIII (continued).

	Cl.	Dif.	Br.	Dif.	I.
Na.....	30.7	5.5	25.2	10.3	14.9
	Dif. 11.0		10.6		10.5
K.....	41.7	5.9	35.8	10.4	25.4
	Dif. 5.1		5.3		5.2
Rb.....	46.8	5.7	41.1	10.5	30.6
	Dif. 8.0		8.2		
Cs.....	54.8	5.5	49.3		
5 Molal, 0°.					
Li.....	18.4	5.2	13.2	9.7	3.5
	Dif. 10.7		10.5		9.9
Na.....	29.1	5.4	23.7	10.3	13.4
Infinite Dilution, 50°.					
Li.....	20.7	6.9	13.8	12.2	1.6
	Dif. 9.3		9.8		10.0
Na.....	30.0	6.4	23.6	12.0	11.6
	Dif. 12.2		11.6		11.8
K.....	42.2	7.0	35.2	11.8	23.4
	Dif. 5.2		5.6		5.1
Rb.....	47.4	6.6	40.8	12.3	28.5
	Dif. 7.6		7.9		8.0
Cs.....	55.0	6.3	48.7	12.2	36.5
1 Molal, 50°.					
Li.....	19.8	6.6	13.2	11.6	1.6
	Dif. 9.3		9.5		9.1
Na.....	29.1	6.4	22.7	12.0	10.7
	Dif. 11.7		11.6		11.7
K.....	40.8	6.5	34.3	11.9	22.4
	Dif. 5.1		5.2		5.3
Rb.....	45.9	6.4	39.5	11.8	27.7
	Dif. 7.9		7.9		7.9
Cs.....	53.8	6.4	47.4	11.8	35.6
3 Molal, 50°.					
Li.....	18.7	6.1	12.6	11.4	1.2
	Dif. 9.1		9.0		9.1
Na.....	27.8	6.2	21.6	11.3	10.3
	Dif. 11.5		11.3		11.3
K.....	39.3	6.4	32.9	11.3	21.6
	Dif. 5.1		5.3		5.2
Rb.....	44.4	6.2	38.2	11.4	26.8
	Dif. 7.8		8.0		7.9
Cs.....	52.2	6.0	46.2	11.5	34.7
5 Molal, 50°.					
Li.....	18.0	5.9	12.1	10.8	1.3
	Dif. 8.8		8.9		8.6
Na.....	26.8	5.8	21.0	11.1	9.9
			Dif. 11.3		11.1
K.....	Dif. 16.6		32.3	11.3	21.0
			Dif. 5.0		5.1

TABLE VIII (continued).

	Cl.	DH.	Br.	DH.	I.
Rb.....	43.4	6.1	37.3	11.2	26.1
Dif.	7.9		8.0		
Cs.....	51.3	6.0	45.3		
Infinite Dilution, 70°.					
Li.....	21.8	7.3	14.5	12.5	2.0
Dif.	33.5		34.0		33.6
Cs.....	55.3	6.8	48.5	12.9	35.6
1 Molal, 70°.					
Li.....	20.4	6.8	13.6	12.1	1.5
Dif.	33.3		33.5		33.3
Cs.....	53.7	6.6	47.1	12.3	34.8
3 Molal, 70°.					
Li.....	19.2	6.5	12.7	11.6	1.1
Dif.	32.9		33.1		33.0
Cs.....	52.1	6.3	45.8	11.7	34.1
5 Molal, 70°.					
Li.....	18.5	6.2	12.3	11.1	1.2
Dif.	32.6		32.8		
Cs.....	51.1	6.0	45.1		

Upon the same assumption as that made in the earlier paper, that at infinite dilution the sum of $a + b$ for lithium iodide is equally distributed between the lithium and iodide ions, Table IX can be constructed to show the change in volume in the formation of the ions from the elements. The values are expressed in cubic centimeters per gram atom and apply at 25°.

TABLE IX.

Li	Na	K	Rb	Cs	I	Br	Cl
-1.4	-12.4	-24.0	-29.1	-37.2	-1.4	-12.7	-19.1

Values at other temperatures are not very different from these. The only apparent regularity in this table is the increase in the values with increasing atomic volume and compressibility in the case of the metals and with increasing compressibility and hydration in the case of the halogens, the atomic volumes of the halogens being all nearly the same.

It is interesting to note the properties of the pairs of elements which according to the above table produce nearly equal contraction. Lithium in the ionic condition is more hydrated, but has a smaller compressibility than iodine, and its atomic volume is only one-half as large; the sodium ion also is more hydrated than the bromine ion, but its compressibility is less than one-third that of bromine, while the two elements have nearly the same atomic volume; the potassium ion is slightly more hydrated than the chlorine ion, but chlorine is three times as compressible and has only half as large an atomic volume.

Where, in general, solution produces contraction, then, since dissociation and probably hydration increase with increasing dilution, the contraction

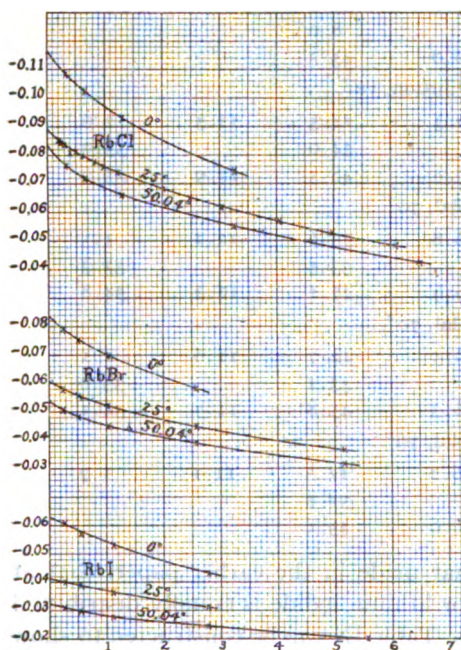


Fig. 8.

as was pointed out in the former paper, such an effect might be caused by the compensating influence of an increasing degree of hydration.

Since the formation of hydrates is undoubtedly hindered by rising temperature, this chief cause of contraction during solution should have less effect at higher temperatures. Hence diminution in volume during solution should become less with rising temperature, while expansion should become greater. Practically this is the case with all the salts except lithium chloride up to 50° , and with most of them up to 70° . Furthermore the changes in volume during solution at 50° and at 70° are not very different.

It is curious, however, that in the case of lithium chloride and bromide the contraction is greater at 50° than at 25° , and that at 100° lithium chloride shows even greater contraction than at 0° . Potassium chloride was the only other salt with which measurements were made at 100° , and here also the results showed contraction greater than at 70° .

Since in both instances the 100° curve is not far from parallel with those obtained at lower temperatures, it is not unreasonable to suppose that the origin of this peculiarity is to be sought in some change in the water itself rather than in one affecting either the ions or the molecules. It

tion during solution should increase with the dilution, as is the case with the greater portion of the salts. On the other hand, wherever expansion occurs during solution, one might expect increasing expansion with increasing dilution. This latter effect actually occurs with only two salts of those which produce expansion during solution, lithium iodide and lithium bromide, and even with these salts only at high concentrations and at temperatures of 25° and above. On the other hand there is no case where there is *diminishing contraction* with increasing dilution.

With lithium bromide and iodide at lower concentrations the expansion during solution diminishes instead of increasing, but,

is on the whole unlikely that so marked a change would affect both the ions and the molecules to a like degree. In this connection it is worth pointing out that several properties of water, for instance, density, specific heat and compressibility, pass through minima with changing temperature. In any event the evidence is too meagre for drawing any certain conclusions as to the cause of this effect. Further work upon change in volume during solution at high temperatures is under way.

At first sight it would seem that one might separate the effects due to the ionized and un-ionized portions, if the degree of dissociation of the salt at different concentrations is known. In fact, an attempt has been made to do this by Heydweiller¹ in recent papers dealing with the properties of solutions of various electrolytes, by the use of the formula:

$$\Delta_s = B_s + (A_s - B_s)i$$

where $\Delta_s = 100(s - 1)/m$, the percentage density difference between solution (s) and water (1) per mol, A_s and B_s represent the separate effects of ionized and un-ionized material, respectively, and i the degree of dissociation.

Heydweiller finds that, using the values for the two constants A_s and B_s in the above equation, the calculated increase in density agrees fairly closely with the observed over a range of concentration between four normal and about half normal, although at lower concentrations marked deviations appear. Heydweiller determines the degree of dissociation at any concentration from the relation of the conductivity to the conductivity at infinite dilution. This method of calculation, obviously, is based on two assumptions of questionable validity: First, it is well known that the degree of dissociation is not accurately given by the relation of the conductivity of a solution to the conductivity at infinite dilution; second, it seems hardly possible that the constants in the above equation are really constants over any considerable range of concentra-

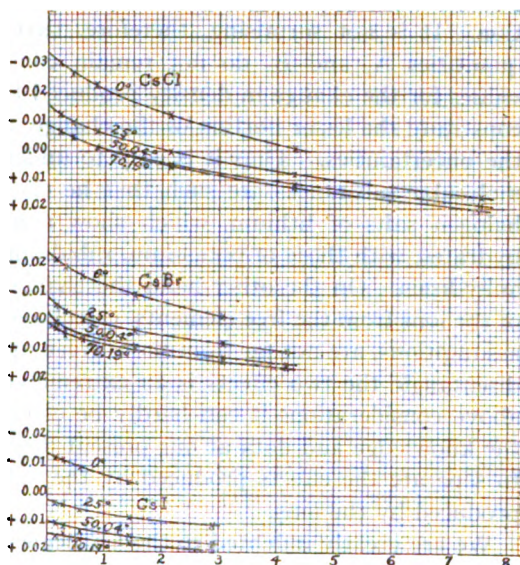


Fig. 9.

¹ *Ann. Physik*, 30, 873 (1909); 37, 739 (1912).

tion, because the degree of hydration of either a molecule or an ion surely changes with the concentration, that is, a change in volume produced by a molecule, or especially an ion, varies with the concentration of the solution. It is not surprising, therefore, that Heydweiller's values for the quantities A_1 and B_1 do not remain constant at high dilutions. The values for the change in density produced by the molecules, because they constitute the lesser portion of the change, are naturally more affected by the uncertainties. Thus it is easy to understand that the values for the molecular substances are such that he classes as similar compounds the halogen salts of lithium, which show marked tendencies to form solid hydrates, with those of potassium, rubidium and cesium, which crystallize anhydrous. On the other hand the change in volume in the production of the ions from the free elements, calculated by Heydweiller¹ upon similar assumptions, are not far from those given upon page 101. This attempt to disentangle the two effects is an extremely interesting one, but from the above considerations it can hardly be considered to be successful. With the knowledge and data at our present disposal, it does not seem possible to separate the effects produced by the molecular substances from those produced by the ions.

We are greatly indebted to the Carnegie Institution of Washington for very generous assistance in this investigation.

Summary.

1. Data are given from which the densities of aqueous solutions of all the halogen salts of the alkali elements at different temperatures may be very exactly calculated.

2. From these data are calculated the changes in volume which take place during the solution of these salts.

3. The explanation of the observed effects, previously proposed upon the basis of Richards's hypothesis of compressible atoms and that of hydration, is supported. This explanation assumes that the following two changes, which take place during solution and dissociation, are the chief causes of the observed effects:

(a) When the molecules dissociate, they are freed in large part from compression due to chemical affinity, with considerable expansion (from 15 to 56% of the original volume of the uncombined elements).

(b) When the ions and probably the molecules are combined with water both the hydrated substance and the water undergo compression. The latter effect varies regularly with the compressibilities of the substances involved as well as with their affinities for each other.

4. The change in volume in the formation of the solution from the free halogens and alkali metals and water is found to be nearly additive at all concentrations; at low concentrations because the changes involved

¹ *Ann. Physik*, 37, 767 (1912).

are chiefly due to the formation of the ions from the elements, which are independent of the salts involved; at high concentrations because the molecules, being less hydrated and less compressible produce smaller contractions, and because the molecular volumes of the salts are very nearly additive.

5. The effect of rising temperature is found in general to diminish contraction or increase expansion owing to lessened hydration of all the substances concerned. Marked exceptions exist at ordinary temperatures in lithium chloride and bromide, and at high temperatures in potassium chloride also.

6. It is pointed out that no simple method exists for separating the effects due to ionized and un-ionized material because of the varying magnitude of the change for each ion or molecule with changing concentration.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF JOHNS HOPKINS UNIVERSITY.]
**THE ACTION OF SALTS WITH WATER OF HYDRATION AND
WITHOUT WATER OF HYDRATION ON THE VELOC-
ITY OF SAPONIFICATION OF ESTERS.¹**

BY J. E. L. HOLMES AND HARRY C. JONES.

Received November 5, 1915.

Jones and Anderson,² in their work on the absorption spectra of solutions, studied the absorption spectra of neodymium chloride in water, in methyl alcohol and in mixtures of these two solvents. They found two sets of absorption spectra corresponding, the one to the aqueous solution and the other to the alcoholic.

In the mixture of these solvents both of these spectra were obtained. Similar results were obtained with neodymium nitrate and praseodymium chloride.

Jones and Strong³ studied a fairly large number of salts in a large number of solvents, and found a large number of "solvent bands." This raised the question whether combined water has different power to absorb light from free water? This was answered by Jones and Guy,⁴ by means of the radiomicrometer. They showed that *combined water was far more transparent than pure water.*

This conclusion was confirmed by the work of Jones, Shaeffer and Paulus.⁵

¹ The results of this investigation are recorded in full in *Publ. Carnegie Inst. Wash.*, No. 230.

² *Publ. Carnegie Inst. Wash.*, No. 110; *Am. Chem. J.*, 41, 163 (1909).

³ *Ibid.*, No. 130 and 160; 43, 37, 224 (1910); 45, 1 (1910); 47, 27 (1912); *Physik. Z.*, 10, 449 (1909); *Phil. Mag.*, April, 1910; *J. chim. phys.*, 8, 131 (1910).

⁴ *Publ. Carnegie Inst. Wash.*, No. 190; *Ann. physik.*, 43, 555 (1914).

⁵ *Physik. Z.*, 15, 447 (1914).

Having found the above physical difference between the action of free and of combined water, the question arose, is there a corresponding chemical difference between water in the combined and in the free state?

Reaction Chosen.

We decided to use the saponification of an ester in the study of the action of free and of combined water for the following reasons:

In the first place, as Berthelot and Saint Gilles¹ had shown, the speed of the reaction is dependent on the relative amounts of the substances used. By keeping the amount of the ester constant we could study the effect of the water in solutions of salts containing the same amounts of water.

Secondly, this reaction proceeds slowly and its velocity could therefore be easily measured.

Thirdly, the speed of the reaction is dependent on the temperature. However, as the temperature rises the hydrates become less complex. From the results obtained with the ester and pure water, as compared with those from solutions of the salts, we could study the effect of rise in temperature on the hydrated salts.

The hydrolysis of the various salts used in this work has been taken into account.

Statement of Problem.

The plan was to investigate the difference in the velocities with which free water and combined water saponified an ester under the following conditions:

- (1) Time and concentration of the salts kept constant, temperature varying.
- (2) Concentration of the salts and temperature constant, time varying.
- (3) Time and temperature constant. Concentration of salts varying.

The conditions were so regulated that the percentage of ester saponified was always small; the H^+ ions of the acid formed being in relatively large numbers as compared with the H^+ ions from water, would in part suppress the ionization of water and effect the saponification themselves.

Experimental.

The reactions were allowed to take place in 100 cc. Jena bottles with ground glass stoppers. These bottles were suspended in constant temperature baths very similar to those employed by Davis and Putnam.²

A concentration was chosen arbitrarily, such that solutions of all the salts to be investigated could be obtained, *i. e.*, two normal. Later it

¹ *Ann. chim. phys.*, 14, 437 (1878); 15, 220 (1878); 65, 385 (1862); 66, 5, 110 (1862); 68, 225 (1865).

² *Publ. Carnegie Inst. Wash.*, No. 210, 117 (1915).

was found to be necessary to change this concentration to normal, using also the more dilute solutions, half-normal and quarter-normal.

The ester first employed was ethyl acetate. After some preliminary work, this was discarded in favor of methyl acetate, since its solubility in some of the strong salt solutions was so slight as to give us a heterogeneous system. Methyl formate was also studied, to see if the results obtained with methyl acetate were of a *general character or specific to the ester in question*. The esters were fractionally distilled several times until they boiled at the proper temperature and their reaction was neutral to indicators. The methyl formate, on account of its apparent instability, had to be frequently redistilled.

The Base and the Indicator.

The finding of the proper base and indicator to be used in titrating the acid formed, gave us quite a little trouble. Sulfuric acid and sodium hydroxide from alcohol did not prove to be satisfactory with phenolphthalein as the indicator. This may have been due in part to the saponification of the ester by the strong base.

The result of an elaborate investigation of indicators, including phenolphthalein, methyl-orange and corallin, and of bases including ammonium, sodium and barium hydroxides, was to show that for our purpose the base to be used was dilute ammonium hydroxide, and the indicator corallin.

To test the accuracy of our method, 0.0733 g. of glacial acetic acid was weighed out and titrated with ammonia, corallin being used as the indicator. The amount of acetic acid calculated from the titration was 0.0730 g. We would then have an error of less than 0.5%. With other organic acids we found errors of less than 0.1%.

Data.

In the following tables of data, the methyl acetate per bottle is 4 cc. or 3.7028 g., the methyl formate, 2 cc. or 1.9402 g. It was found that calcium chloride and potassium nitrate on dilution increase, then decrease the velocity of the reaction. Duplicate measurements were therefore made with new solutions. It was at this point that we decided to study also methyl formate. The volumes of the solutions of the salts that contained 30 cc. of water were calculated, the water per cc. of the solution being the difference in weight between 1 cc. of the solution and the salt in 1 cc. The water used in preparing the solutions of the salts, bases, and acid, had been carefully purified and had a mean specific conductivity of 1.5 times 10^{-6} at 25°. This water was also used in recrystallizing the salts. In the tables of data the concentrations of the solutions of the salts are expressed as N , $N/2$, and $N/4$. Tables I, II, III, IV, and V give the percentages of the methyl acetate saponified, Tables VI, VII and VIII of the methyl formate. Duplicate measurements were made with fresh solutions of magnesium sulfate and strontium

TABLE I.—METHYL ACETATE.

Solutions. N.	15°		25°		35°		25°		35°		25°	
	24 hours.	25° 48 hours.	24 hours.	25° 48 hours.	24 hours.	25° 48 hours.	24 hours.	25° 48 hours.	24 hours.	25° 48 hours.	Solutions. N/4.	25° 24 hours.
1.....	{ 30 cc. H ₂ O }	0.076	0.147	0.390	0.287	{ 30 cc. H ₂ O }	0.145	0.386	{ 30 cc. H ₂ O }	0.153		
2.....	{ 30.87 cc. KCl }	0.076	0.145	0.392	0.289	{ 30.48 KCl }	0.144	0.385	{ 30.27 KCl }	0.152		
3.....	{ 31.23 cc. KNO ₃ }	0.100	0.224	0.720	0.516	{ 30.66 cc. KNO ₃ }	0.206	0.669	{ 30.48 cc. KNO ₃ }	0.196		
4.....	{ 30.84 cc. CaCl ₂ }	0.100	0.222	0.722	0.513	{ 30.39 cc. CaCl ₂ }	0.206	0.666	{ 30.24 cc. CaCl ₂ }	0.198		
5.....	{ 30.60 cc. MgCl ₂ }	0.099	0.194	0.611	0.431	{ 30.39 cc. MgCl ₂ }	0.201	0.612	{ 30.24 cc. MgCl ₂ }	0.177		
6.....	{ 30.87 cc. SrCl ₂ }	0.097	0.196	0.614	0.431	{ 30.45 cc. SrCl ₂ }	0.201	0.613	{ 30.27 cc. SrCl ₂ }	0.177		
7.....		0.119	0.387	1.68	1.03		0.400	1.35		0.278		
8.....		0.117	0.385	1.69	1.05		0.398	1.36		0.277		
9.....		0.132	0.410	1.67	1.33		0.326	1.23		0.276		
10.....		0.134	0.411	1.67	1.30		0.323	1.23		0.276		
11.....		0.130	0.378	1.41	0.992		0.297	1.12		0.236		
12.....		0.128	0.375	1.42	0.989		0.297	1.12		0.239		

TABLE II.—METHYL ACETATE.

Solutions. N.	15°		25°		35°		25°		35°		25°	
	24 hrs.	25° 48 hrs.	24 hrs.	25° 48 hrs.	24 hrs.	25° 48 hrs.	24 hrs.	25° 48 hrs.	24 hrs.	25° 48 hrs.	Solutions. N/4.	25° 24 hrs.
1 H ₂ O, 30 cc.	0.083	0.154	0.394	0.296	H ₂ O, 30 cc.	0.153	0.391	H ₂ O, 30 cc.	0.152			
2 LiCl, 30.96 cc.	0.094	0.204	0.626	0.462	LiCl, 30.48 cc.	0.199	0.590	LiCl, 30.24 cc.	0.194			
3 KNO ₃ , 31.29 cc.	0.099	0.215	0.631	0.457	KNO ₃ , 30.60 cc.	0.213	0.632	KNO ₃ , 30.39 cc.	0.212			
4 NaCl, 30.57 cc.	0.109	0.247	0.808	0.590	NaCl, 30.30 cc.	0.241	0.746	NaCl, 30.21 cc.	0.222			
5 CaCl ₂ , 30.87 cc.	0.129	0.393	1.72	1.15	CaCl ₂ , 30.39 cc.	0.306	1.35	CaCl ₂ , 30.27 cc.	0.285			
6 Ca(NO ₃) ₂ , 31.59 cc.	0.129	0.330	1.32	0.860	Ca(NO ₃) ₂ , 30.69 cc.	0.310	1.12	Ca(NO ₃) ₂ , 30.36 cc.	0.270			

TABLE III.—METHYL ACETATE.

Solutions, N.	15°.		35°.		25°.		Solutions, N/4.	
	24 hrs.	25°. 24 hrs.	35°. 24 hrs.	25°. 24 hrs.	25°. 24 hrs.	25°. 24 hrs.		
1 H ₂ O, 30 cc.	0.086	0.155	0.394	0.296	0.153	0.394	H ₂ O, 30 cc.	0.153
2 NaNO ₃ , 30.93 cc.	0.105	0.225	0.692	0.490	0.223	0.663	NaNO ₃ , 30.36 cc.	0.210
3 NaBr, 30.84 cc.	0.104	0.228	0.703	0.517	0.222	0.660	NaBr, 30.24 cc.	0.210
4 KBr, 31.11 cc.	0.107	0.230	0.690	0.507	0.224	0.667	KBr, 30.39 cc.	0.216
5 BaCl ₂ , 30.93 cc.	0.142	0.377	1.38	0.967	0.315	1.09	BaCl ₂ , 30.24 cc.	0.267
6 Mg(NO ₃) ₂ , 31.48 cc.	0.126	0.326	1.35	0.883	0.285	1.13	Mg(NO ₃) ₂ , 30.36 cc.	0.261

TABLE IV.—METHYL ACETATE.

Solutions, N.	15°.		35°.		25°.		Solutions, N/4.	
	24 hrs.	25°. 24 hrs.	35°. 24 hrs.	25°. 24 hrs.	25°. 24 hrs.	25°. 24 hrs.		
1 H ₂ O, 30 cc.	0.086	0.155	0.395	0.296	0.155	0.395	H ₂ O, 30 cc.	0.155
2 KI, 31.53 cc.	0.090	0.038	0.057	0.048	0.073	0.172	KI, 30.43 cc.	0.136
3 NaI, 31.20 cc.	0.075	0.119	0.341	0.239	0.171	0.498	NaI, 30.30 cc.	0.176
4 CaBr ₂ , 31.26 cc.	0.075	0.134	0.653	0.492	0.153	0.689	CaBr ₂ , 30.33 cc.	0.191
5 MgSO ₄ , 30.18 cc.	0.095	0.166	0.406	0.346	0.150	0.372	MgSO ₄ , 30.12 cc.	0.138
6 Sr(NO ₃) ₂ , 31.56 cc.	0.139	0.297	1.09	0.711	0.287	0.968	Sr(NO ₃) ₂ , 30.36 cc.	0.260

TABLE V.—METHYL ACETATE.

Solutions, N.	15°.		35°.		25°.		Solutions, N/4.	
	24 hrs.	25°. 24 hrs.	35°. 24 hrs.	25°. 24 hrs.	25°. 24 hrs.	25°. 24 hrs.		
1 H ₂ O, 30 cc.	0.087	0.153	0.392	0.297	0.153	0.392	H ₂ O, 30 cc.	0.153
2 LiBr, 30.81 cc.	0.033	0.053	0.128	0.100	0.105	0.307	LiBr, 30.21 cc.	0.161
3 Li ₂ SO ₄ , 30.75 cc.	0.103	0.153	0.306	0.278	0.149	0.297	Li ₂ SO ₄ , 30.18 cc.	0.139
4 BaBr ₂ , 31.47 cc.	0.081	0.179	0.705	0.445	0.223	0.813	BaBr ₂ , 30.39 cc.	0.241
5 SrBr ₂ , 31.47 cc.	0.075	0.096	0.250	0.190	0.130	0.387	SrBr ₂ , 30.39 cc.	0.164
6 LiNO ₃ , 31.02 cc.	0.086	0.167	0.508	0.370	0.182	0.555	LiNO ₃ , 30.33 cc.	0.201

TABLE VI.—METHYL FORMATE.

		25°. 4 hrs.	15°. 8 hrs.	Solutions. N/2.	15°. 4 hrs.	Solutions. N/4.	15°. 4 hrs.
1	H ₂ O, 30 cc.	0.668	3.89	H ₂ O, 30 cc.	0.680	H ₂ O, 30 cc.	0.667
2	LiBr, 30.81 cc.	0.309	5.26	LiBr, 30.45 cc.	0.650	LiBr, 30.21 cc.	0.927
3	Li ₂ SO ₄ , 30.75 cc.	0.742	3.80	Li ₂ SO ₄ , 30.36 cc.	0.667	Li ₂ SO ₄ , 30.18 cc.	0.618
4	BaBr ₂ , 31.47 cc.	0.754	9.27	BaBr ₂ , 30.75 cc.	1.05	BaBr ₂ , 30.39 cc.	1.42
5	SrBr ₂ , 31.47 cc.	0.278	3.47	SrBr ₂ , 30.72 cc.	0.590	SrBr ₂ , 30.39 cc.	0.990
6	LiNO ₃ , 31.02 cc.	0.865	6.74	LiNO ₃ , 30.54 cc.	1.02	LiNO ₃ , 30.33 cc.	1.11

TABLE VII.—METHYL FORMATE.

1	H ₂ O, 30 cc.	0.661	3.87	H ₂ O, 30 cc.	0.680	H ₂ O, 30 cc.	0.680
2	NaBr, 30.87 cc.	1.05	7.00	NaBr, 30.42 cc.	0.988	NaBr, 30.21 cc.	0.927
3	KCl, 30.90 cc.	1.11	7.05	KCl, 30.45 cc.	1.11	KCl, 30.27 cc.	1.05
4	BaCl ₂ , 30.93 cc.	1.78	13.71	BaCl ₂ , 30.48 cc.	1.71	BaCl ₂ , 30.24 cc.	1.47
5	Ca(NO ₃) ₂ , 31.59 cc.	1.24	9.86	Ca(NO ₃) ₂ , 30.69 cc.	1.17	Ca(NO ₃) ₂ , 30.36 cc.	1.11
6	MgSO ₄ , 30.18 cc.	1.36	8.50	MgSO ₄ , 30.15 cc.	1.10	MgSO ₄ , 30.12 cc.	0.926

TABLE VIII.—METHYL FORMATE.

1	H ₂ O, 30 cc.	0.670	3.89	H ₂ O, 30 cc.	0.661	H ₂ O, 30 cc.	0.680
2	KI, 31.56 cc.	0.192	2.14	KI, 30.81 cc.	0.494	KI, 30.42 cc.	0.667
3	CaBr ₂ , 31.26 cc.	0.618	8.59	CaBr ₂ , 30.54 cc.	0.982	CaBr ₂ , 30.33 cc.	1.03
4	SrCl ₂ , 30.87 cc.	2.55	17.44	SrCl ₂ , 30.45 cc.	1.98	SrCl ₂ , 30.27 cc.	1.64
5	CaCl ₂ , 30.87 cc.	2.97	19.86	CaCl ₂ , 30.39 cc.	2.18	CaCl ₂ , 30.27 cc.	1.85
6	Mg(NO ₃) ₂ , 31.48 cc.	2.52	17.92	Mg(NO ₃) ₂ , 30.66 cc.	2.02	Mg(NO ₃) ₂ , 30.36 cc.	1.75

bromide, since the results obtained with these salts were very low as compared with the results from the other salts that contain a large amount of water of crystallization. The results found were, however, practically identical with those earlier obtained. In Table I duplicate results are given to show how concordant they were. Duplicate results were obtained in every case, but to economize space only one set is given.

Discussion of Results.

From Plates I and II, the salts which produce the greatest increase in velocity, and which have the largest temperature coefficients are magnesium chloride, calcium chloride, strontium chloride, barium chloride, magnesium nitrate, calcium nitrate, and strontium nitrate. All of these salts crystallize with water of crystallization, varying from six to two molecules each. Next come salts that do not have water of crystallization, as sodium chloride, sodium nitrate, potassium chloride and potassium bromide. Along with these salts we have some that have water of crystallization as sodium bromide, calcium bromide, lithium chloride, lithium bromide, lithium nitrate and magnesium sulfate, which seem to be exceptions in the light of the action of the other salts that crystallize with water.

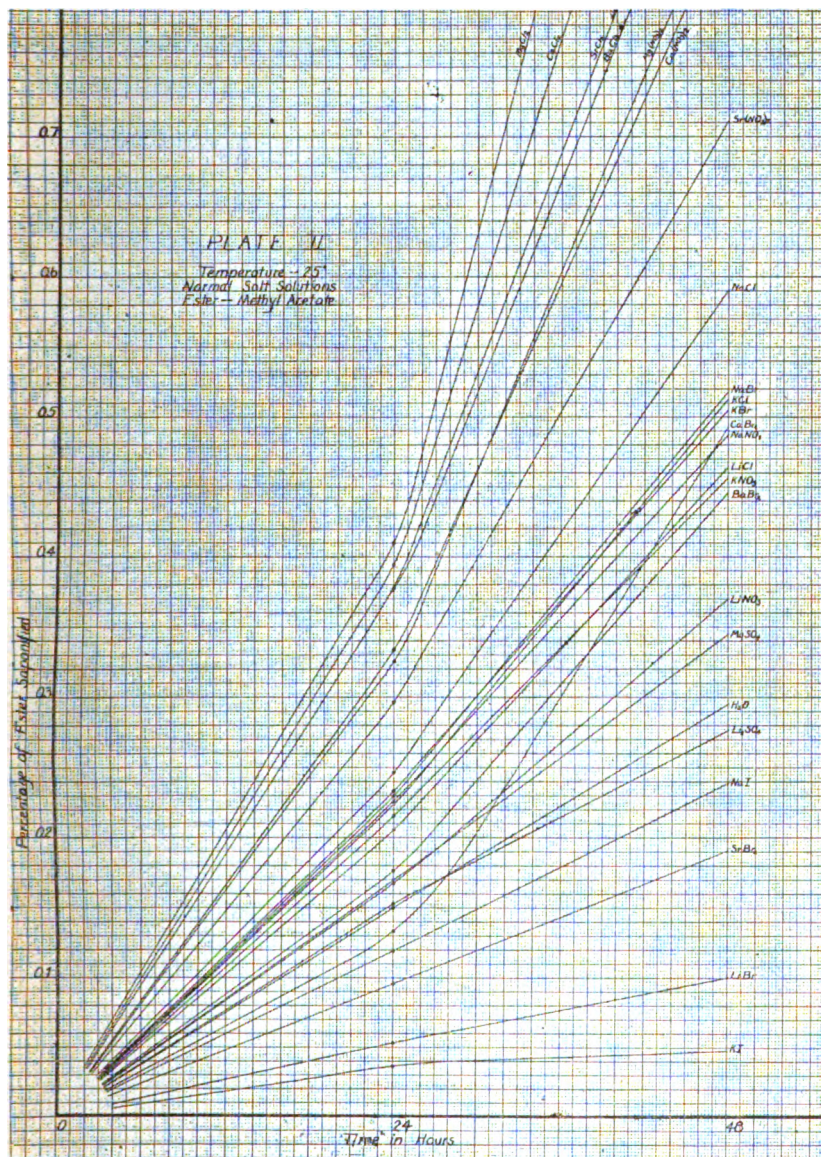
Still more inexplicable seem to be the curves for lithium sulfate, sodium iodide, strontium bromide, lithium bromide and potassium iodide, since these curves are below the curve for pure water.

Let us now consider Plate III. As the dilution is increased, salts such as magnesium chloride show a marked decrease in velocity, the salts with no water of crystallization showing a less decrease, while the apparent exceptions, such as calcium bromide, strontium bromide, etc., show a marked increase in velocity, most of their curves ending above the curve for water.

Let us now consider the salts of any one metal (Plates I and II), *e. g.*, calcium. The chloride increases the velocity more than the nitrate, the nitrate more than the bromide. With potassium and sodium, the chloride has more effect than the nitrate, the nitrate more than the bromide, the bromide more than the iodide. Of the salts studied, the sulfates seem to have least effect. There also seems to be a general relation between the metals themselves, as magnesium, calcium, strontium and barium, though in the series lithium, sodium and potassium, lithium seems to be an exception.

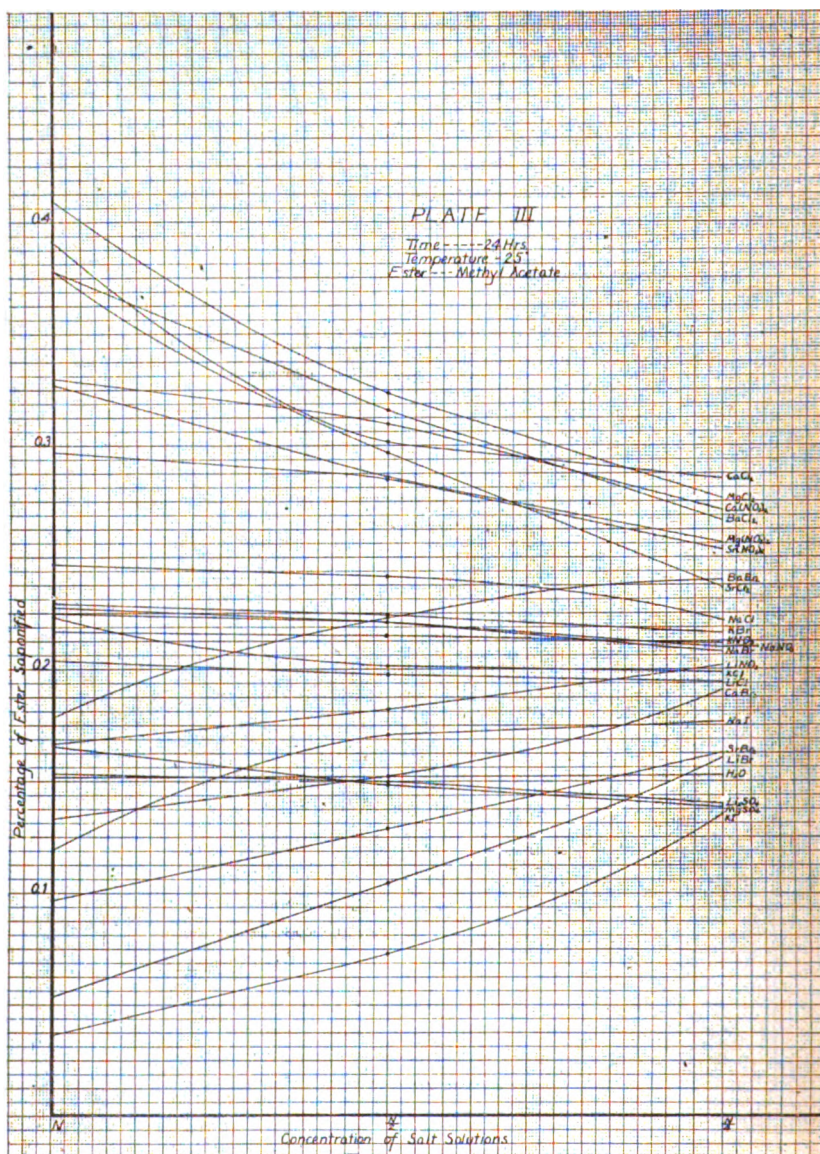
The curves for the methyl formate are of the same general character, the only difference being that the curves are more extended, more being above the curve for water, probably due to the larger amount of saponification. The curves for calcium bromide, barium bromide and magnesium sulfate with methyl formate do not seem to be exceptions, since they fall above the curves for salts with no water of crystallization.

salt on the reaction velocity. With more dilute solutions of potassium iodide (0.25 N) the velocity of the reaction is increased. Kellogg's



curves for strontium chloride, calcium chloride, and barium chloride show that the cation must also be taken into account. A possible explanation of the behavior of barium bromide, calcium bromide, etc.,

may be that the total effect, due to these salts, is due to a combination between a cation tending to increase the velocity and an anion tending to decrease it.

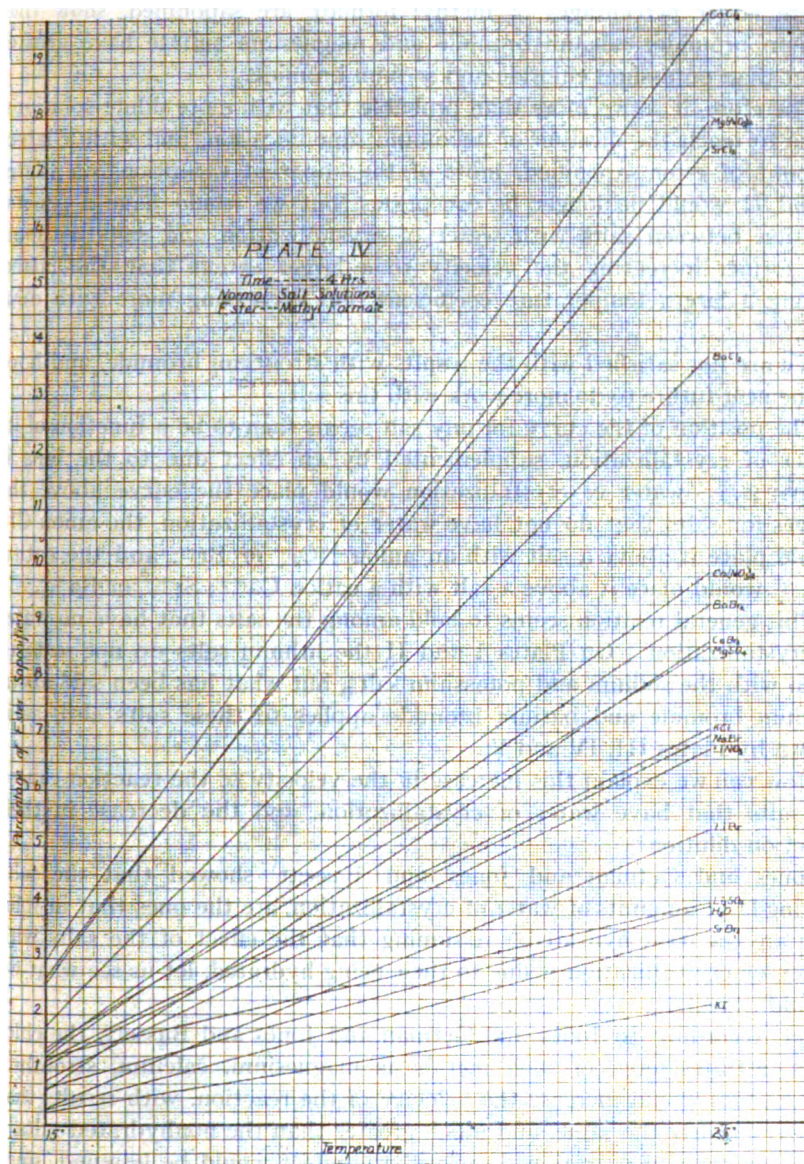


Kellogg¹ also finds that there is a concentration for each salt that will produce the greatest increase in the velocity of the reaction. Still further

¹ *Loc. cit.*

increase or decrease of the concentration from this point, diminishes the velocity of the reaction.

The action of the apparent exceptions in the study of this problem,



i. e., lithium nitrate, lithium bromide, calcium bromide, etc., may be due to the concentration of maximum saponification not having been reached, since these salts all increase the velocity on dilution.

Altogether, it is probable that had the dilution been still farther increased, the apparent exceptions would have proved not to be exceptions at all. This seems to be all the more true in that the curves of Plate IV, where larger percentages of methyl formate are saponified, show that barium bromide, calcium bromide and magnesium sulfate have greater effect than potassium chloride and sodium bromide.

Therefore, it seems more than probable that with more dilute solutions, so as to reach the dilution of maximum saponification, and with a larger amount of ester saponified, most of the apparent exceptions on Plates I and II would no longer be exceptions, but we would have a general relation between salts with water of crystallization and salts without; the former increasing the velocity to a larger extent than the latter, having a larger temperature coefficient and decreasing more with dilution.

We are not satisfied with the results with strontium bromide, and hope in the near future to do more work with this salt.

The position of the curve for any salt seems then to be a function of its water of crystallization, supplemented by an effect due to the ions it forms; *e. g.*, water of crystallization would place the curve above the curves for salts that do not have water of crystallization, the anion Cl^- would place it above a salt with an anion NO_3^- or Br^- ; and the cation Mg^{++} would place it above a salt with a cation Ca^{++} , Sr^{++} or Ba^{++} .

This general relation seems to hold among the salts that have no water of crystallization. On Plates I and II the lithium salts do not seem to fit in with the sodium and potassium salts, but what has been said about calcium bromide and barium bromide applies to these salts also, as is shown by Plates III, IV and V.

How can we explain this increase in the velocity of the reaction caused by salts that have water of crystallization, and the decrease in their effect on dilution?

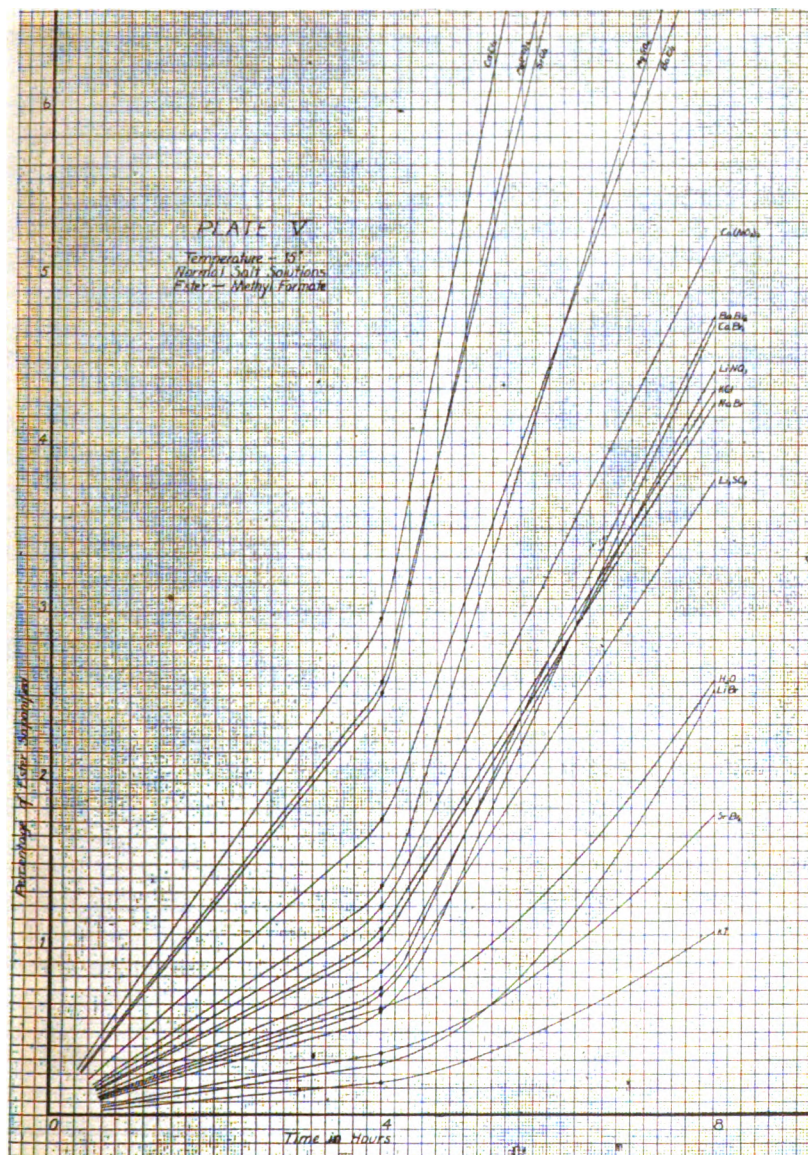
Jones and Getman and Jones and Bassett¹ showed that the salts having large amounts of water of crystallization, are the ones that in solution are the most hydrated. Assuming that the effect of the salts with water of crystallization is due to their being hydrated, let us see what we should expect.

(1) According to Jones and Getman and Jones and Bassett, the chlorides, nitrates, etc., of such metals as magnesium, calcium, strontium and barium would increase the velocity of the reaction, with results that are very nearly the same, and much greater than the nonhydrated salts.

(2) As the concentration decreases, the effect would be lessened, since the total combined water would be less, the decrease being much more rapid than in the case of nonhydrated salts.

¹ *Publ. Carnegie Inst. Wash.*, No. 60, 15.

(3) From the work of Jones and Pearce,¹ who showed that the hydrating power of a cation is an inverse function of its atomic volume, we

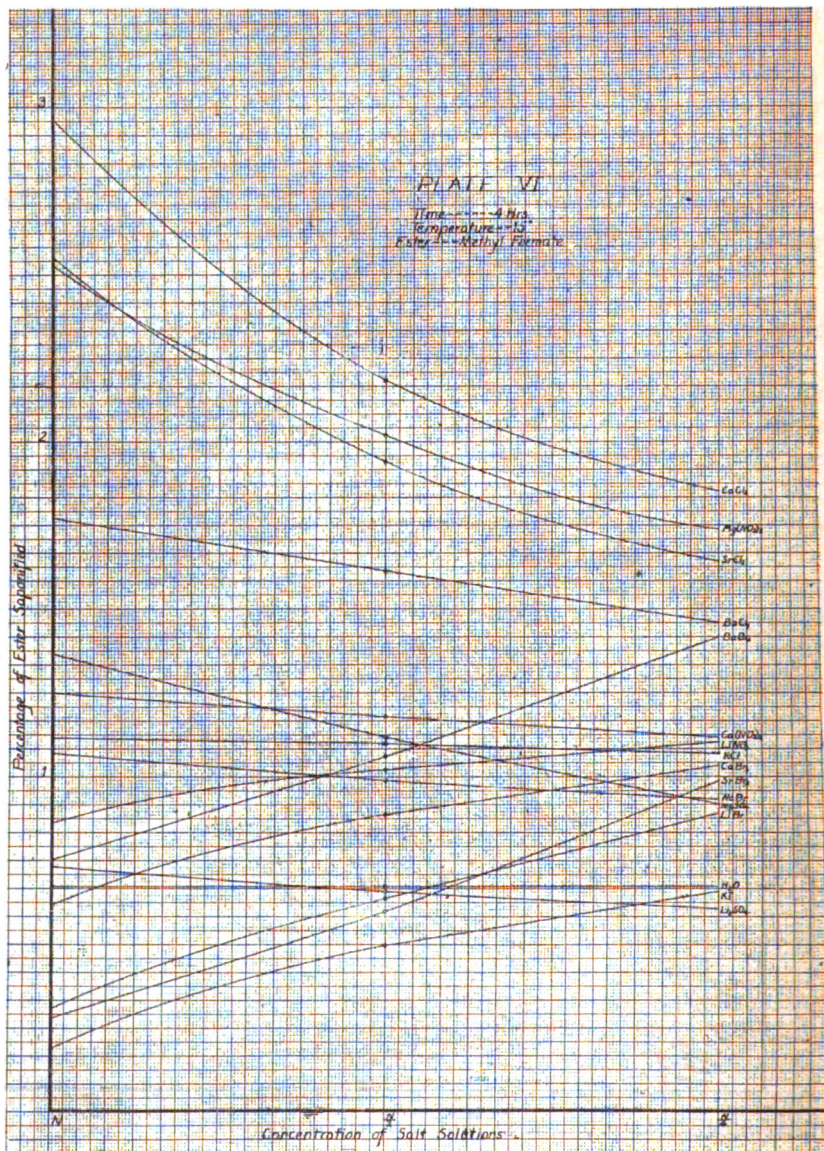


should expect the curves for the salts of magnesium, calcium, barium and strontium with a common anion, to be similar to those found by him,

¹ Publ. Carnegie Inst. Wash., No. 180, 57 (1913).

i. e., magnesium salts having the greatest effect, then calcium, strontium and barium.

Let us see if the experimental data confirm these conclusions, based



on the assumption that the difference in action between salts that have water of crystallization and salts that do not, is due primarily to the hydrates formed by the salts with water of crystallization.

Taking into consideration the facts brought out earlier, that the dilution of maximum saponification for the apparent exceptions had not been reached, and that larger percentages of ester saponified would also tend to make the apparent exceptions not real, we can draw from the curves the following conclusions:

(1) Salts with water of crystallization increase the velocity of the reaction much more than salts without water of crystallization.

(2) The effect of salts with water of crystallization decreases on dilution much more than that of salts without water of crystallization.

(3) Among the metals with common anions as magnesium, calcium, strontium and barium chlorides or nitrates, the curves arrange themselves in the order of the decreasing atomic weights of the cations.

We, therefore, conclude that the difference in action between salts with water of hydration and salts without, on the saponification of esters, is due primarily to the chemical difference between free and combined water.

As an explanation of this difference in action we venture the suggestion that the combined water¹ is more highly ionized than free water; and with hydrated salts, we have this effect added to the salt effect shown in the case of nonhydrated salts.

Pearce² shows that the cations are the ones that are hydrated; the anions, if hydrated at all, are only slightly so.

The curves for the halides of potassium show that in the saponification of esters, the anions play an important part. This is in line with what Kellogg³ found.

Therefore, it seems probable that the anions are also hydrated to a certain extent.

But how can the larger temperature coefficient of reaction velocity of the hydrated salts be accounted for, since, with rise in temperature the hydrates become less complex? A study of Plates II and V shows that, temperature being constant, the amounts of ester saponified in the presence of the hydrated salts, as the time increases, is much greater than the amounts saponified in the presence of the nonhydrated salts.

This is probably due to the larger amount of acid formed by the saponification of the ester by combined water. With rise in temperature the larger amount of acid would give us a larger temperature coefficient. Another factor to be taken into consideration is the *hydrolysis* of the hydrated salts which, though small at low temperature, increases greatly as the temperature rises. The increased fluidity of the solution must also be taken into account, the hydrates becoming less complex with rise in temperature. These three factors would probably offset

¹ Since this was written it has been confirmed by Palmaer and Melander, *Z. Elektrochem.*, 21, 418 (1915).

² *Publ. Carnegie Inst. Wash.*, No. 180, 57 (1913).

³ *Loc. cit.*

the decomposition of the hydrates, giving less combined water, with the result that we would have a larger temperature coefficient of reaction velocity for the hydrated than for the nonhydrated salts.

From the standpoint of hydrates breaking down with rise in temperature, let us consider the effect of such rise in temperature on chemical reactions in general. The influence of temperature on the velocity of reactions is usually very great.

Berthelot¹ showed that the velocity with which an ester is formed is about twenty-two thousand times as great at 200° as at 7°.

Spohr² finds that cane sugar is inverted five times as rapidly at 55° as at 25°. Various attempts have been made to explain the effect of rise in temperature on the velocity of chemical reactions. A decrease in the viscosity of the medium with rise in temperature, allowing the ions to move more rapidly; a decrease in the mass of the ion with rise in temperature, and the increased kinetic energy of the molecules and ions, have been cited as the causes of the great increase, with rise in temperature, in reaction velocity. None of these theories seem sufficient to account for such an increase in the velocity of reactions as was noticed by Berthelot and others.

From the solvate theory of solution we see that ions and molecules attract to them molecules of the solvent. We would expect these ions to react more slowly, especially if the solvate were very complex, since the solvate would act as a protective covering around the ions and diminish the velocity with which they would react with one another. But suppose the temperature is raised, the solvate would become less and less complex, until finally the ions would not have any appreciable protective covering. In such a case, where the ions are in direct contact, we would expect the velocity of the reaction to be greatly increased.

We, therefore, suggest that this is one of the more important causes of the increase in the velocity of chemical reactions with rise in temperature.

In conclusion, we can say that the *chemical differences between free and combined water*, brought out in the study of this problem, are strictly analogous to the physical differences between free and combined water as shown by their power to absorb light, which led us to investigate this problem.

Summary.

The following conclusions have either been confirmed or brought out in this investigation:

(1) The reaction involving the decomposition of an ester proceeds slowly at ordinary temperatures and, therefore, can be readily and accurately studied.

¹ *Essai de Mécanique Chimique*, 2, 93 (1879).

² *Z. physik. Chem.*, 2, 195 (1888).

(2) The hydrolysis of the chlorides and nitrates, etc., of calcium, magnesium, strontium and barium employed in the study of this problem, is so small that it alone cannot account for the results obtained.

(3) Salts with water of crystallization increase the velocity of the saponification of an ester to a greater extent than salts with no water of crystallization.

(4) On dilution, the effect with salts having water of crystallization decreases more rapidly than with salts without crystal water, which shows that the result cannot be due to hydrolysis alone.

(5) The curves for the saponification of methyl formate are very similar to those for methyl acetate.

(6) The large effect of salts with water of crystallization is probably due, in part, to their being hydrated, combined water being more highly ionized than free water.

(7) The amount of the saponification, and, therefore, the position of the curve seems to be due to the combined effect of both cation and anion.

(8) It is probable that anions as well as cations are somewhat hydrated.

(9) The hydration of cations is inversely proportional to their atomic volumes.

(10) There seems to be a dilution of maximum saponification for each salt.

(11) Hydrated salts show a large temperature coefficient, notwithstanding the decomposition of hydrates with rise in temperature, probably due in part to hydrolysis.

(12) Decomposition of hydrates may play an important role in the increased velocity of chemical reactions with rise in temperature.

(13) The chemical differences between free and combined water are analogous to the physical differences.

Further work is now in progress in this laboratory on this problem. Certain apparent discrepancies in this preliminary communication are being further investigated, and other lines of attack opened up.

BALTIMORE, MD.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY.]

CONDUCTIVITIES OF CERTAIN ORGANIC ACIDS IN ABSOLUTE ETHYL ALCOHOL.

BY H. H. LLOYD, JOHN B. WISEL, AND HARRY C. JONES.¹

Received August 30, 1915.

During the past six years a fairly thorough and systematic study of the conductivity and dissociation of aqueous solutions of organic acids, as

¹ The results of this investigation are recorded in full in *Publ. Carnegie Inst. Wash.*, No. 230 (1915).

affected by temperature as well as by dilution, has been in progress in this laboratory.¹ In view of the fact that very little work had been done upon solutions of organic acids in absolute ethyl alcohol, it was decided to extend our investigations into this field.² Accordingly Wightman, Wiesel and Jones undertook a preliminary investigation of the problem, worked out a fairly satisfactory method of procedure and made conductivity measurements of nine organic acids.³ The present investigation is a continuation and extension of their work.

Experimental.

Reagents.—Absolute alcohol was prepared in the manner described by Wightman, Wiesel and Jones.⁴ It never contained more than 0.04% water, and its specific conductivity averaged 2×10^{-7} .

The organic acids were obtained from two well-known firms. The same methods of purifying them were employed as when the conductivities of these acids were determined in aqueous solution.⁵ After purification they were carefully dried in a vacuum desiccator containing sulfuric acid. Whenever practicable the melting point (of the acids) was taken as one criterion of purity.

Aqueous solutions of ammonia were used for titration purposes, since ammonia had been found by Wightman, Wiesel and Jones⁶ to give the most satisfactory results. Corallin (rosolic acid) was used as the indicator, because it is sensitive to ammonia and to organic acids, and is not sensitive to carbon dioxide except when the latter is present in fairly large quantity. The endpoint with corallin is not quite as sharp and distinct as with phenolphthalein, and considerable practice is necessary before reliable results can be obtained.

Apparatus.—On account of the high resistance of the alcoholic solutions of the acids it was found necessary to make use entirely of the cylindrical type of conductivity cell. The method of obtaining the constants of these cells was described by White⁷ and by Wightman.⁸

Since the percentage temperature coefficients of conductivity for substances dissolved in alcohol, as well as the coefficient of expansion of the alcohol itself, are so large, it is necessary to regulate the temperature as closely as possible. This was done by the combination of a specially devised gas regulator and thermoregulator. These have already been

¹ *Publ. Carnegie Inst. Wash.*, No. 170, Part II (1912); No. 210, Chapter II (1915).

² *Am. Chem. J.*, 44, 156 (1910); 46, 56 (1911); 48, 320, 411 (1912); 50, 1 (1913).

³ *THIS JOURNAL*, 36, 2243 (1914); *Publ. Carnegie Inst. Wash.*, No. 210, Chapter III (1915).

⁴ *THIS JOURNAL*, 36, 2246 (1914).

⁵ *Am. Chem. J.*, 44, 156 (1910); 46, 56 (1911); 48, 320, 411 (1912); 50, 1 (1913).

⁶ *THIS JOURNAL*, 36, 2247-9 (1914).

⁷ *Am. Chem. J.*, 42, 527 (1909).

⁸ *Ibid.*, 44, 64 (1911).

described in a paper by Davis and Hughes.¹ The constant temperature baths employed were of the improved form designed by Dr. Davis,² of this laboratory. In these baths ordinarily the temperature does not vary more than 0.01° , which is sufficiently constant for our purpose. With greater precautions as to insulation against changes in temperature, and with further modification of the thermoregulator, the variation can be decreased to a few thousandths of a degree. The thermometers employed were of the differential Beckmann type, and were carefully compared with a standard Reichsanstalt thermometer, which had been calibrated also at the United States Bureau of Standards. The resistance box which was used throughout this entire investigation had also been calibrated at the Bureau of Standards. A very fine Kohlrausch slide-wire bridge was employed, by means of which it was possible to read distances on the slide-wire corresponding to tenths of a millimeter (the total length of the wire was five meters). Flasks, pipets and burets for measuring purposes were in all cases carefully calibrated.

Procedure.—The solutions of organic acids in alcohol were made up in 200 cc. Jena measuring flasks calibrated for 25° .³ A portion of each solution was removed to fill the conductivity cells and the remainder was used for the titrations, which were made simultaneously with the conductivity measurements. At first thought it would seem probable that keeping the solutions in the flasks at a constant temperature (25°), and subjecting the solutions in the cells to changes in temperature (15 – 35°), would produce a change in the rates of esterification. If this were true, the normalities of the solutions in the cells would be different from the values obtained by the titration of the solutions in the flasks, and a considerable error would be introduced. It was found, however, that there was no appreciable difference in the amount of acid present at any moment in a given solution, whether the solution was kept in the 25° bath continuously for 8 hours or whether it was transferred from one bath to another during this time. The reason for this is to be found no doubt in the slow rate at which esterification takes place under the conditions of this investigation.

Although it is fairly certain, then, that variation in the temperature has no measurable effect upon the rate of esterification in alcoholic solutions of the organic acids, this variation does alter to a considerable extent the volume, and therefore the concentration of these solutions. For example, a solution which has a volume of 1000 cc. at 25° contracts to 989.23 cc. when cooled to 15° , and expands to 1011.14 cc. when warmed to 35° . Because of this fact a correction has to be applied to the volume calculated

¹ *Z. physik. Chem.*, 85, 519 (1913).

² *Publ. Carnegie Inst. Wash.*, No. 210, 121 (1915).

³ *Cf. THIS JOURNAL*, 36, 2247 (1914).

from titration, before molecular conductivity can be estimated at 15° and 35° . This correction was made in the following way: Let us suppose that the normality of a given solution at 25° , as determined by titration against ammonia, is N_{25} . The normality at 15° , N_{15} , would then be expressed by the ratio $N_{25}/0.98923$, and the true volume at 15° (*i. e.*, the number of liters which contain a gram molecular weight of the dissolved acid) would be the reciprocal of this ratio, or $0.98923/N_{25}$. Similarly, the normality at 35° would be $N_{25}/1.01114$ and the volume would be $1.01114/N_{25}$.

Results.

In the following tables of conductivity results, V_m is the volume at which the solutions were made up; V_c is the corrected volume. The corrections were applied in the manner just described, both for expansion or contraction of the alcohol and for change in the concentration of the acid due to formation of ester. Molecular conductivity, μ , was calculated in the usual manner.

Acid.	MOLECULAR CONDUCTIVITIES.					
	V_m	V_c	μ 15°	V_c	μ 25°	V_c μ 35°
Phenyl acetic	8	7.94	0.004176	8.04	0.005660	8.13 0.007325
	32	32.70	0.01122	33.42	0.01614	34.08 0.02167
	128	146.9	0.04392	152.2	0.06347	156.9 0.08598
	512	537.9	0.1581	545.0	0.2245	552.2 0.2976
Oxyisobutyric	8	7.99	0.005234	8.08	0.006666	8.17 0.008346
	32	32.71	0.01429	33.33	0.01813	33.84 0.02264
	128	139.5	0.05022	143.3	0.06391	147.3 0.07969
	512	537.6	0.1699	543.8	0.2208	550.1 0.2718
Bromo-palmitic	8	7.97	0.007014	8.06	0.009027	8.16 0.01142
	32	33.07	0.01776	33.52	0.02316	33.99 0.02964
	128	151.8	0.07013	154.9	0.09248	158.1 0.1183
	512	540.0	0.2349	546.1	0.3129	552.5 0.3950
Malonic	8	8.12	0.0190	8.13	0.0237	8.18 0.0319
	32	32.9	0.0434	33.2	0.0555	33.7 0.0737
	128	129.3	0.0775	129.5	0.0985	129.6 0.1351
	512	512.8	0.2533	514.9	0.3160	518.1 0.4338
Ethylmalonic	8	7.96	0.01937	8.05	0.02590	8.15 0.03346
	32	32.28	0.06333	32.70	0.08345	33.13 0.1066
	128	134.9	0.2459	137.1	0.3236	140.6 0.4134
	512	532.4	0.9924	538.5	1.295	545.1 1.624
Diethylmalonic	8	7.95	0.02857	8.05	0.03860	8.14 0.05022
	32	32.25	0.06042	32.66	0.08044	33.04 0.1054
	128	136.0	0.1257	139.1	0.1732	142.2 0.2279
	512	533.3	0.2527	539.4	0.3441	546.0 0.4494
Propylmalonic	8	7.95	0.03271	8.04	0.04220	8.13 0.05280
	32	32.21	0.07995	32.63	0.1049	33.09 0.1326
	128	136.0	0.2739	139.1	0.3663	141.4 0.4628
	512	533.3	1.021	539.4	1.346	545.7 1.692

MOLECULAR CONDUCTIVITIES (*continued*).

Acid.	V_m	V_c	μ_p 15°	V_c	μ_p 25°	V_c	μ_p 35°
Dipropylmalonic	8	8.12	0.03354	8.22	0.04453	8.33	0.05772
	32	31.29	0.06759	31.84	0.09058	32.45	0.1178
	128	130.3	0.1416	131.9	0.1889	133.6	0.2442
	512	540.3	0.3031	548.8	0.4078	558.3
Butylmalonic	8	7.97	0.0169	8.08	0.0219	8.19	0.0277
	32	32.89	0.0269	33.65	0.0363	34.26	0.0479
	128	142.3	0.0549	147.8	0.0794	153.2	0.1069
	512	535.0	0.1257	547.6	0.1780	555.0	0.2364
Allylmalonic	8	7.97	0.01309	8.06	0.01757	8.15	0.02304
	32	33.07	0.02867	33.52	0.03882	34.01	0.05068
	128	142.4	0.08701	145.2	0.1170	148.6	0.1491
	512	540.6	0.2822	546.7	0.3756	553.4	0.4798
Benzylmalonic	8	7.95	0.03391	8.04	0.04200	8.13	0.05155
	32	32.23	0.04880	32.64	0.06189	33.04	0.07738
	128	134.7	0.1043	137.1	0.1361	139.4	0.1723
	512	533.0	0.3017	539.1	0.4032	545.7	0.5091
Monobromosuccinic	8
	32	33.02	0.0426	33.65	0.0556	34.26	0.0736
	128	150.1	0.0827	157.1	0.1177	162.5	0.1589
	512	539.1	0.2167	546.4	0.3087	553.4	0.4112
Dibromosuccinic	8	7.96	0.01839	8.06	0.02441	8.16	0.03213
	32	32.31	0.03648	32.76	0.04816	33.15	0.06206
	128	136.4	0.09984	139.1	0.1289	142.2	0.1654
	512	533.3	0.3130	539.4	0.4051	546.0	0.5105
Sebacic	8	8.71	0.001794	8.83	0.002411	8.95	0.003141
	32	34.20	0.004001	34.79	0.005566	35.44	0.007549
	128	138.7	0.01387	140.6	0.01884	142.6	0.02510
	512	579.5	0.04694	593.1	0.06465	605.1	0.08592
Thiodiglycolic	8	8.65	0.02326	8.76	0.02951	8.88	0.03746
	32	33.95	0.03263	34.57	0.04269	35.15	0.05557
	128	138.1	0.05261	140.0	0.07042	141.7	0.09281
	512	568.2	0.1119	579.7	0.1501	587.5	0.2015
Benzilic	8	7.96	0.01660	8.05	0.02200	8.14	0.02799
	32	32.17	0.05527	32.56	0.07267	33.04	0.09271
	128	134.0	0.2176	137.1	0.2882	141.0	0.3711
	512	531.8	0.8849	537.9	544.8	1.217
Maleic	8	7.95	0.1504	8.04	0.1922	8.14	0.2400
	32	32.24	0.2913	32.86	0.3768	33.38	0.4736
	128	136.3	0.5977	139.8	0.7806	145.1	1.0034
	512	532.7	1.184	540.5	1.537	546.8	1.932
Fumaric	8	7.98	0.00471	8.09	0.00629	8.19	0.00815
	32	32.66	0.00941	33.20	0.01291	33.79	0.01710
	128	140.3	0.0282	144.8	0.0392	145.8	0.0515
	512	535.0	0.0920	543.2	0.1276	550.4	0.1668

MOLECULAR CONDUCTIVITIES (*continued*).

Acid.	V_m .	V_c .	μ_g 15°.	V_c .	μ_g 25°.	V_c .	μ_g 35°.
Itaconic	8	7.95	0.01452	8.05	0.01946	8.14	0.02504
	32	32.25	0.05870	32.74	0.07795	33.20	0.09963
	128	133.0	0.2413	135.6	0.3214	137.9	0.4100
	512	532.1	0.9737	538.5	1.2762	545.1	1.531
Mesaconic	8	8.11	0.006683	8.22	0.008393	8.36	0.01044
	32	31.67	0.01264	32.47	0.01636	33.16	0.02059
	128	130.5	0.03132	132.6	0.04005	134.6	0.05074
	512	551.1	0.1080	564.3	0.1405	575.5	0.1784
Phenylpropionic	8	7.95	0.01797	8.04	0.02240	8.13	0.02712
	32	32.23	0.03400	32.61	0.04278	32.99	0.05181
	128	135.3	0.06868	137.5	0.08641	139.8	0.1070
	512	532.4	0.1535	538.8	0.1932	545.1	0.2478
Aconitic	8	7.95	0.01359	8.45	0.01757	8.15	0.02238
	32	33.06	0.02529	33.63	0.03403	34.26	0.04481
	128	150.1	0.06649	155.6	0.09492	164.2	0.1309
	512	539.1	0.1838	545.2	0.2606	551.9	0.3471
Benzoic	8	7.945	0.002892	8.05	0.004073	8.15	0.005444
	32	32.62	0.009884	32.99	0.01405	33.51	0.01893
	128	137.3	0.04311	143.3	0.06205	149.7	0.08563
	512	536.7	0.1583	544.7	0.2233	552.2	0.2960
<i>m</i> -Chlorbenzoic	8	7.94	8.04	0.005422	8.15	0.007153
	32	32.84	0.01136	33.40	0.01610	33.79	0.02149
	128	147.8	0.04907	151.7	0.06978	157.4	0.09523
	512	537.9	0.1829	545.0	0.2556	552.2	0.3402
<i>m</i> -Nitrobenzoic	8	7.98	0.005725	8.08	0.007470	8.17	0.009575
	32	32.65	0.01786	33.07	0.02308	33.54	0.02915
	128	140.8	0.07293	143.5	0.09414	146.9	0.1178
	512	537.9	0.2754	544.1	0.3526	550.7	0.4362
1,3,5-Dinitrobenzoic	8	7.95	0.01947	8.04	0.02554	8.13	0.03290
	32	32.28	0.03083	32.72	0.04113	33.15	0.05377
	128	135.6	138.7	141.4
	512	532.7	0.4427	538.8	0.4980	545.1	0.6192
Picric	8	8.69	2.934	8.80	3.502	8.91	4.120
	32	34.02	5.202	34.64	6.264	35.15	7.392
	128	138.3	9.569	140.3	11.445	142.2	13.484
	512	570.8	18.192	585.8	22.031	597.3	26.106
Sulfosalicylic	8	7.97	16.63	8.06	8.15	25.63
	32	32.24	26.60	32.68	30.68	33.14	34.87
	128	137.6	36.46	140.7	42.81	143.9	50.06
	512	533.0	40.18	539.4	44.35	546.0	55.94
<i>o</i> -Aminobenzoic	8	7.98	0.03531	8.07	0.04290	8.17	0.05160
	32	32.62	0.02760	33.07	0.03400	33.53	0.04242
	128	139.9	0.05148	142.7	0.06279	145.5	0.07697
	512	534.4	0.1817	540.5	0.2092	546.9

MOLECULAR CONDUCTIVITIES (*continued*).

Acid.	V _m .	V _c .	μ , 15°.	V _c .	μ , 25°.	V _c .	μ , 35°.
<i>p</i> -Aminobenzoic	8	7.95	0.2020	8.05	0.2427	8.14	0.2897
	32	32.36	0.2397	32.80	0.2910	33.23	0.3512
	128	138.1	0.2665	141.4	0.3331	143.8	0.4128
	512	533.3	0.2165	539.7	0.2672	545.7	0.3231
<i>o</i> -Toluic	8	7.98	0.005429	8.08	0.006721	8.17	0.008174
	32	32.63	0.01299	33.07	0.01637	33.48	0.01992
	128	140.0	0.04298	142.7	0.05680	144.7	0.06917
	512	537.3	0.1230	543.5	0.1745	549.8	0.2078
<i>p</i> -Toluic	8	7.95	0.001288	8.04	0.001648	8.13	0.002163
	32	32.27	0.003453	32.68	0.004444	33.09	0.005923
	128	136.0	0.01387	138.3	0.01770	141.4	0.02588
	512	532.7	0.04262	539.1	0.05283	545.7	0.06930
Cinnamic	8	7.97	0.001370	8.06	0.001782	8.16	0.002350
	32	32.81	0.003612	33.28	0.004603	33.85	0.006222
	128	141.6	0.01297	144.0	0.01660	146.9	0.02205
	512	535.1	0.04243	541.4	0.04737	548.3	0.06585
Phthalic	8	7.95	0.02880	8.04	0.03945	8.14	0.05217
	32	32.23	0.07932	32.63	0.1077	33.02	0.1401
	128	136.4	0.2804	138.7	0.3771	141.8	0.4847
	512	533.6	1.043	539.7	1.378	546.3	1.747
Dichlorophthalic	8
	32	33.73	0.05056	34.32	0.06579	34.99	0.08331
	128	138.1	0.08203	139.8	0.1047	141.4	0.1315
	512	568.2	0.1386	579.7	0.1803	588.6	0.2313
Anisic	8	7.97	0.01259	8.06	0.01662	8.15	0.02118
	32
	128	142.0	0.2173	144.8	0.2880	146.9	0.3625
	512	539.7	0.8025	545.8	1.052	552.2	1.255
Mandelic	8	8.10	0.005370	8.20	0.007273	8.30	0.009553
	32	32.60	0.01232	33.01	0.01680	33.57	0.02216
	128	129.2	0.03256	130.8	0.04303	132.6	0.05529
	512	455.2	0.09377	498.0	0.1389	504.8	0.1787
Camphoric	16	15.91	0.006475	16.11	0.008957	16.32	0.01138
	64	64.49	0.01058	65.79	0.01539	66.92	0.01907
	256	272.1	0.02258	291.5	0.03236	309.4	0.04301
	1024	1159.0	0.04637	1176.0	0.06706	1191.0	0.09171

Discussion of the Results.

The most striking feature of the conductivities of the organic acids in alcohol, as shown by an examination of the foregoing tables, is their *extremely small value*. In nearly all cases, the conductivities are several hundred times smaller than the conductivities of the same acids in water. When we consider the fact that alcohol has from one-fourth to one-fifth the dissociating power of water, as shown by the dissociation of strong

electrolytes in these solvents, the above fact does not at present seem to admit of any very satisfactory explanation.

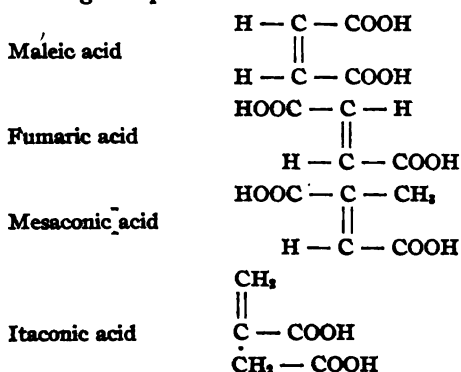
The effect of increase in the dilution is to increase the molecular conductivity. The increase in conductivity in many cases is almost proportional to the volume.

A knowledge of the extent to which organic acids are dissociated in alcoholic solution would be highly desirable. It is hoped that a method for the determination of percentage dissociation will be worked out in the near future. Goldschmidt¹ obtained values for the limiting conductivities of several organic acids in alcohol from the μ_{∞} values of their sodium salts. These varied from 83 to 93, depending on the nature of the acid. It has not yet been found practicable to determine the limiting conductivities of the organic acids studied in this investigation, but as a result of Goldschmidt's work it is certain that they do not differ greatly from 90. If this be the case, the dissociation of the organic acids studied by the authors, as determined by conductivity, do not, in any case, exceed 2% even in $N/512$ solutions.

Relation between Composition and Conductivity.

In his classical study of the conductivity of aqueous solutions of organic acids, to which reference has already been made, Ostwald² pointed out a number of relations between composition and molecular conductivity. The general validity of these relations has been confirmed by the work which has been in progress in this laboratory for the past fifteen years. In view of this, an examination of the results obtained for alcoholic solutions, in the attempt to discover similar relations, should prove to be interesting.

Take the following compounds:



The conductivity of maleic acid is many times that of fumaric. This

¹ *Z. Elektrochem.*, 15, 4 (1909); 20, 473 (1914); *Z. physik. Chem.*, 70, 627 (1910); 81, 30 (1912); 89, 129 (1914).

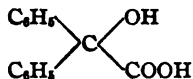
² *Z. physik. Chem.*, 3, 170, 241, 369 (1889).

fact is in keeping with the results obtained in aqueous solution,¹ and with the present-day conception of the configuration of these acids. Mesoconic acid is a methyl substitution product of fumaric acid, and its conductivity is of the same order of magnitude as that of the fumaric acid. Itaconic acid, which is isomeric with mesaconic, but which has very different constitution, shows much higher conductivity. Malonic acid, at a volume at 32 and at 25°, has a molecular conductivity of 0.055. Under the same conditions, ethylmalonic acid has a conductivity of 0.083; diethylmalonic, 0.080; propylmalonic, 0.105; dipropylmalonic, 0.090; butylmalonic, 0.036; allylmalonic, 0.039; and benzylmalonic, 0.062.

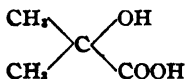
The above results show that the introduction of an ethyl group increases the conductivity, while the introduction of a second ethyl group tends to decrease the conductivity of ethylmalonic acid. Propylmalonic acid has uniformly higher conductivity than ethylmalonic, and the conductivity of the dipropyl acid is uniformly higher than that of the diethyl. Just as diethylmalonic acid has smaller conductivity than ethylmalonic, so, dipropylmalonic acid has smaller conductivity than propylmalonic.

Butylmalonic acid and allylmalonic acid, at the dilution in question, have smaller conductivities than malonic acid itself; but as the dilution increases, the conductivity of allylmalonic acid becomes greater than that of malonic acid.

Benzylmalonic acid has greater conductivity than malonic acid, but less than ethylmalonic acid. This is especially interesting, in consideration of the fact that, in general, a phenyl derivative of an acid has much greater conductivity than the corresponding methyl derivative; *e. g.*, the conductivity of acetic acid in alcohol is so small that it cannot be accurately measured. On the other hand, benzoic acid has a conductivity of 0.014. Again, benzilic acid having the formula



has a much greater conductivity than the corresponding methyl derivative, oxyisobutyric acid

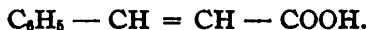


This is in keeping with the results obtained for these acids in aqueous solution,² and with the general observation that the replacement of a methyl group by a phenyl group increases the conductivity.

Phenylpropionic acid $\text{C}_6\text{H}_5 - \text{C} = \text{C} - \text{COOH}$ has a conductivity many times larger than that of cinnamic acid

¹ *Publ. Carnegie Inst. Wash.*, No. 170, 113 (1912).

² *Ibid.*, No. 170, 115, 132 (1912).



This is in accord with what was found for these same acids in aqueous solutions.

Take the following series:

Benzoic acid,	$\text{C}_6\text{H}_5\text{COOH}.$
<i>m</i> -Chlorobenzoic acid,	$\text{C}_6\text{H}_4\text{ClCOOH}.$
<i>m</i> -Nitrobenzoic acid,	$\text{C}_6\text{H}_4\text{NO}_2\text{COOH}.$
1,3,5-Dinitrobenzoic acid,	$\text{C}_6\text{H}_3(\text{NO}_2)_3\text{COOH}.$
<i>o</i> -Toluic acid,	$\text{C}_6\text{H}_4\text{CH}_3\text{COOH}.$
<i>p</i> -Toluic acid,	$\text{C}_6\text{H}_4\text{CH}_3\text{COOH}.$

The conductivities of benzoic acid and of *o*-toluic acid are about equal, whereas the conductivity of *p*-toluic acid is very much less. That the same relation holds also for other substituent groups may be seen from the results obtained a year ago by Wightman, Wiesel and Jones.¹ For example, the conductivity of *o*-chlorobenzoic acid and of *o*-nitrobenzoic acid are approximately the same as that of benzoic, but the conductivities of the corresponding para-acids are considerably less.

It is a well established fact that in aqueous solution the conductivity of benzoic acid is somewhat increased by the introduction of methyl, chlorine, or the nitro group, in the para position; and enormously increased by the introduction of one of these groups in the ortho position. In contradistinction to this, the effect of these groups upon the conductivity in alcoholic solution appears to be negative. Just the opposite is true if the chlorine or nitro group occupies the meta position. In these cases the conductivity of benzoic acid is somewhat increased.

The introduction of a second nitro group into *m*-nitrobenzoic acid still further increases the conductivity. While benzoic acid $\text{C}_6\text{H}_5\text{COOH}$ has a

conductivity of only 0.015, phthalic acid $\text{C}_6\text{H}_4 \begin{matrix} \swarrow \text{COOH} \\ \searrow \text{COOH}(o) \end{matrix}$ a dicarboxy

derivative, has a conductivity of 0.108, which is seven times as great. This same relation holds in aqueous solutions.²

Of all the acids studied in this investigation, with one exception, picric acid, $\text{C}_6\text{H}_3(\text{NO}_2)_3\text{OH}$ is the strongest. The only stronger acid in alcoholic solutions is sulfosalicylic, which has a conductivity approaching that of hydrochloric acid in this solvent. This is in general analogous to what was found when these compounds were dissolved in water,³ sulfosalicylic acid in water having almost exactly the same conductivity as hydrochloric acid in that solvent.

In order to compare the conductivities of the above named organic

¹ THIS JOURNAL, 36, 2251-2252 (1914).

² Publ. Carnegie Inst. Wash., No. 170, 116, 133 (1912).

³ Ibid., 170, 120, 121 (1912).

acids in alcohol, with the conductivities of these same compounds in water, reference must be had to *Publication of the Carnegie Institution of Washington*, No. 170 (1912).

BALTIMORE, MD.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS.]

ON THE ACTION OF CERTAIN ACID REAGENTS ON THE SUBSTITUTED UREAS AND THIAZOLE.

[SECOND PAPER.]

By F. B. DAINS, R. C. ROBERTS AND R. Q. BREWSTER.

Received November 13, 1915.

This is a continuation of an investigation¹ begun several years ago on the reactivity of the anilido hydrogen in the oxygen and sulfur ureas and is a study of the effect of acyl reagents on the grouping —NHCO(S)NH— or NH—C=NR in both open-chain and ring compounds.

SR

Disubstituted Ureas and Acid Chlorides.—As has been previously shown, a urea of the type RNHCONHR reacts with an acid chloride at $150\text{--}160^\circ$ giving the amidine hydrochloride, RNH—C=NR , HCl and

R

carbon dioxide. An acyl derivative of the urea is first formed. This then dissociates into carbanilide and an isocyanate, $\text{RNHCOR} + \text{RNCO}$, which at the temperature employed react giving carbon dioxide and the amidine.²

Molecular proportions of benzoyl chloride and di-*o*-tolylurea were heated in a sealed tube at 170° for four hours. The tube opened with pressure, due to carbon dioxide and hydrogen chloride, while the odor of isocyanate could be detected in the escaping gases. The solid contents of the tube consisted of benz-*o*-toluide and the hydrogen chloride salt of a base, which was freely soluble in water. The base, benz-di-*o*-tolylamidine, $\text{C}_6\text{H}_5\text{—C=NC}_7\text{H}_7(\text{NHC}_7\text{H}_7)$ was precipitated with sodium hydroxide and purified by crystallization from alcohol, in which it is easily soluble. It separated in fine, white needles melting at $87\text{--}8^\circ$.

Calc. for $\text{C}_{21}\text{H}_{20}\text{N}_2$: N, 9.33%. Found: 9.44%.

Diphenylurea and isovaleryl chloride react at 140° giving a base, isovaler-diphenylamidine, which melts at 103° . It was identified by the analysis of the yellow platinum salt, which has a melting point of 207° .

Calc. for $(\text{C}_{17}\text{H}_{20}\text{N}_2)_2\text{H}_2\text{PtCl}_6$: Pt, 21.35%. Found: 21.22%, 21.44%.

¹ THIS JOURNAL, 22, 181 (1900).

² *Ibid.*, 22, 188 (1900).

The picrate of this base melts at 144–5°. This is possibly identical with the amidine obtained by Hofmann¹ as a result of heating isovaleric acid, anilin and phosphorus trichloride. His product melted at 111°.

Di-*m*-tolylurea and isovaleryl chloride were heated in a sealed tube at 140–50°. From the reaction product was isolated the base, isovaler-di-*m*-tolylamidine, which crystallizes in fine, white needles melting at 102°.

Calc. for $C_{18}H_{24}N_2$: N, 10.00%. Found: 10.64%.

The yellow platinum salt melts at 214°.

Calc. for $(C_{18}H_{24}N_2)_2H_2PtCl_6$: Pt, 20.01%. Found: 20.09%.

From di-*p*-tolylurea and isovaleryl chloride was obtained isovaler-di-*p*-tolylamidine, white crystals from alcohol with a melting point of 91–2°.

Calc. for $C_{18}H_{24}N_2$: N, 10.00%. Found: 9.86%.

The amidine hydrochloride melts at 175° and the platinum salt at 199°.

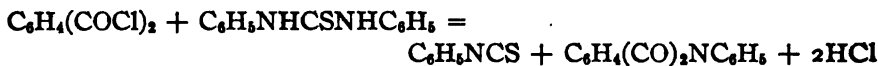
Calc. for $(C_{18}H_{24}N_2)_2H_2PtCl_6$: Pt, 20.01%. Found: 20.19%.

Under like conditions, molar proportions of di-*p*-tolylurea and *m*-nitrobenzoyl chloride gave *m*-nitrobenz-*p*-toluide and the base *m*-nitrobenz-di-*p*-tolylamidine. This separates from alcohol in fine, yellow needles, which melt at 137°.

Calc. for $C_{21}H_{19}O_2N_3$: N, 12.18%. Found: 12.27%.

Thioureas and Acid Chlorides.—Previous investigations have shown² that the substituted thioureas and acid chlorides may react with the formation of an acyl derivative of the urea, a molecular addition product of the urea and the acid chloride, or at an elevated temperature with the production of a mustard oil and a substituted acid amide. Additional evidence is afforded by the following experiments: Thus at 90°, acetyl chloride and di- α -naphthylthiourea give α -naphthyl mustard oil and α -acetnaphthalide, while at 160° the same urea reacts with benzoyl chloride with the formation of the mustard oil and α -benznaphthalide. Only traces of a basic product are formed.

Corresponding results are obtained when a diacid chloride is used. When a molar mixture of thiocarbanilide and phthalyl chloride is heated at 160°, the main products are phenyl mustard oil and phthalanil in accordance with the following equation:



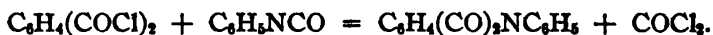
A small amount of triphenylguanidine is also formed, as a result probably of the action of hydrogen chloride on the thiocarbanilide.

Under like conditions, phthalyl chloride and diphenyl urea give chiefly phthalanil, although the odor of phenyl isocyanate as well as phosgene

¹ Hofmann, *Jahresb.*, 1865, 416.

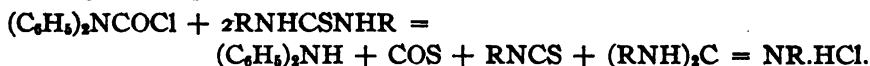
² Deninger, *Ber.*, 28, 1332 (1895); Dixon, *J. Chem. Soc.*, 101, 2522 (1912); Dains, *THIS JOURNAL*, 22, 191 (1900).

was noted on opening the tube. It would seem that at 160° the isocyanate was capable of reacting with the acid chloride giving phthalanil and carbonyl chloride.



No amidine formation occurs as in the case of the simple acid chloride.

Thioureas and Urea Chlorides.—Dixon¹ found that when thiocarbanilide was heated with methyl phenyl urea chloride, there resulted phenyl mustard oil and triphenyl guanidine. Some years ago, before Dixon's work appeared, the action of diphenyl urea chloride on certain thioureas was tried, and as the results confirm the investigation of Dixon, they will be briefly noted. Thiocarbanilide and diphenyl urea chloride react easily and smoothly at $110\text{--}120^{\circ}$ with the formation of carbonyl sulfide, phenyl mustard oil, triphenyl guanidine and diphenylamine, according to the general equation



Under like conditions, the urea chloride and di-*p*-tolylthiourea gave *p*-tolyl mustard oil and tri-*p*-tolyl guanidine, while from di-*o*-tolylthiourea was isolated the corresponding mustard oil and guanidine. The guanidines were identified by their melting points and the analysis of their platinum salts.

That the oxygen ureas behave in a similar manner was shown by the fact that when diphenylurea and diphenylurea chloride were heated at 170° in a sealed tube, the products were carbon dioxide, phenyl isocyanate and triphenyl guanidine.

The trisubstituted thioureas, compounds of the type R_3NCSNHR , contain an anilido hydrogen which can be easily replaced by an acyl group. Thus Dixon and Taylor² have shown that α,β -diphenyl- α -methylthiourea and benzoyl chloride form an addition product, which readily loses hydrogen chloride yielding benzoyl-diphenyl-methyl-thiourea, a stable compound not easily desulfurized.

The same ease of replacement was noticed in the case of diphenyl-ethyl-thiourea and carbonyl chloride. To a benzene solution of the thiourea (two mols) and pyridine (two mols) was added a molar solution of phosgene in benzene. The solution became warm and pyridine hydrochloride was deposited. From the benzene solution was isolated a compound, which crystallizes from alcohol in fine, white needles, melting at 166° . The analysis gave figures corresponding to carbonyl bis-diphenyl-ethyl-thiourea, $\text{CO}(\text{NC}_6\text{H}_5\text{CSNC}_6\text{H}_5.\text{C}_2\text{H}_5)_2$.

Calc. for $\text{C}_{20}\text{H}_{20}\text{ON}_4\text{S}$: N, 10.41%. Found: 10.62%, 10.50%.

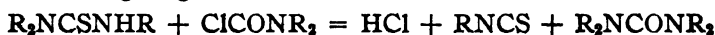
¹ *J. Chem. Soc.*, 75, 405 (1899).

² *Ibid.*, 101, 2522 (1912).

It is not desulfurized by boiling with mercuric oxide in benzene solution.

Urea Chlorides and Tri-substituted Thioureas. Synthesis of Tetra-substituted Oxygen Ureas.—Efforts to bring about reaction between the trisubstituted thioureas and urea chloride in solution, even in the presence of pyridine, have thus far proved fruitless. Dixon¹ met with the same success, as he found that benzyl-phenyl-ethyl-thiourea was not affected by diphenyl urea chloride in a boiling chloroform solution.

However, when higher temperatures are used the following general reaction occurs, giving a mustard oil and a tetra-substituted urea:



Molar quantities of diphenyl-methyl-thiourea and diphenyl urea chloride were heated in an oil bath at 150°. From the reaction product was obtained phenyl mustard oil and a sulfur free compound melting at 105°. It was readily soluble in alcohol and proved to be triphenyl-methyl-urea, $(C_6H_5)_2NCONC_6H_5 \cdot CH_3$.

Calc. for $C_{20}H_{18}ON_2$: 9.27%. Found: 9.44%, 9.45%.

Under like conditions, diphenyl-methyl-thiourea and phenyl methyl urea chloride gave phenyl mustard oil and diphenyl-dimethyl-urea, identical with the product obtained by Michler and Zimmermann.²

From diphenyl-ethyl-thiourea and diphenyl urea chloride was obtained the phenyl mustard oil and triphenyl-ethyl urea (m. p. 79°).³

Equal mols of diphenyl-ethyl-thiourea and phenyl methyl urea chloride react at 150–60° yielding the mustard oil and α, β -diphenyl- α, β -methyl-ethyl urea. It was purified by crystallization from gasoline and is easily soluble in alcohol and benzene, sparingly so in ether. It melts at 74°.

Calc. for $C_{18}H_{18}O_2N$: 11.02%. Found: 11.15%, 11.35%.

The same urea was prepared and its constitution thus proven, by heating a mixture of phenyl-ethyl-amine, phenyl methyl urea chloride and pyridine at 140°.

Isothiourea Ethers and Acid Chlorides.—In a previous paper,⁴ results were obtained which indicated that the anilido hydrogen of isothiourea ethers of the type, $RN = C(NHR)SR$, could be easily replaced by an acyl group. The following experimental work substantiates this view. The methyl ether of isothiodiphenyl urea was heated at water bath temperature for fifteen minutes with a little more than one equivalent of acetic anhydride, the resulting light yellow liquid was dissolved in alcohol, diluted with water and allowed to stand and the white solid which gradually precipitated re-dissolved in hot dilute alcohol from which it separated.

¹ *J. Chem. Soc.*, **75**, 399 (1899).

² *Ber.*, **12**, 1166 (1879); *Jahrb.*, **1881**, 335.

³ *Ber.*, **9**, 712 (1876); **14**, 2185 (1881).

⁴ *THIS JOURNAL*, **22**, 196 (1900).

in cubical crystals melting at 71° . It proved to be the methyl ether of acetyl-isothiodiphenyl urea, $C_6H_5N = C - N(COCH_3)C_6H_5$.



Calc. for $C_{16}H_{15}ON_2S$: N, 9.78%. Found: 9.90%, 10.04%.

The addition of the acetyl group has greatly reduced the basic properties of the isothiurea ether. The acyl derivative is only slightly soluble in dilute acids. It does not form a solid hydrochloride, when hydrogen chloride is passed into its benzene solution, nor does it give a picrate. Alkalies split off the acetyl group giving the original ether. It is more stable, however, than the corresponding acetyl derivative of the simple thiocarbanilide, since that dissociates above its melting point into mustard oil and acetanilide.

Methyl acetyl-isothiodiphenyl urea is readily soluble in chloroform, benzene and gasoline, but only moderately so in ether.

The same acetyl derivative can be easily prepared by adding acetyl chloride (one mol) to a benzene solution of the methyl ether (two mols) and allowing the mixture to stand. On examination the supernatant liquid was found to contain the acetyl compound, while the solid residue consisted of the hydrogen chloride salt of the original methyl isothiurea ether.

The Ethyl Ether of *m*-Nitrobenzoyl Isothio-di-*o*-tolyl-urea, $C_7H_7N : C - S - C_2H_5$,

$\begin{array}{c} | \\ C_7H_7 - N - COC_6H_4NO_2 \end{array}$.—Molecular quantities of the ethyl ether and

pyridine (to unite with the hydrogen chloride) were dissolved in benzene and the *m*-nitro-benzoyl chloride slowly added. After filtering from the pyridine hydrochloride, the evaporation of the benzene solution gave the nitro-benzoyl derivative, which after recrystallization melted at 122° .

Calc. for $C_{24}H_{21}O_2N_3S$: N, 9.70%. Found: 9.85%, 9.90%.

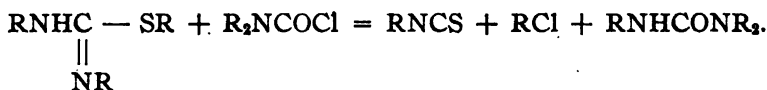
The compound is not basic and is readily decomposed by boiling alcoholic potash, giving ethyl mercaptan, di-*o*-tolyl urea and *m*-nitro-benzoic acid.

Under like conditions the methyl ether of isothiodiphenyl urea, pyridine and *m*-nitro-benzoyl chloride gave the methyl ether of *m*-nitro-benzoyl-isothio-diphenyl urea. Purified from gasoline, it melts at 101° .

Calc. for $C_{22}H_{17}O_2N_3S$: N, 10.70%. Found: 10.51%, 10.60%.

The Isothiurea Ethers and Urea Chlorides.—From the ease of substitution of an acyl group in the isoureaethers and the general stability of the molecule, it was thought that there might be a possibility of introducing the grouping R_2NCO in place of the anilido hydrogen in these compounds. All efforts to bring about combination at the temperature of boiling benzene were without success, while at higher temperatures the

following reaction was found to occur with the formation of an alkyl chloride, mustard oils and a trisubstituted urea.



The methyl ether of isothio-diphenyl urea and diphenyl urea chloride were heated in a sealed tube at 150° for four hours. The tube opened with pressure, due to methyl chloride and the odor of mercaptan was noticeable. From the contents of the tube were isolated phenyl mustard oil and methyl-diphenyl urea, white crystals from gasoline, melting at 106° .

Calc. for $\text{C}_{14}\text{H}_{14}\text{ON}_2$: N, 12.41%. Found: 12.63%.

It was further identified by its synthesis from aniline and methyl phenyl urea chloride. The same urea was obtained by Gebhardt¹ from phenyl isocyanate and mono-methyl aniline.

***o*-Tolyl-methyl-phenyl Urea.**—The ethyl ether of isothio-*o*-tolyl urea and methyl phenyl urea chloride were heated at 150° with the resulting formation of ethyl chloride, *o*-tolyl mustard oil and *o*-tolyl methyl phenyl urea, $\text{C}_7\text{H}_7\text{NHCON}(\text{CH}_3)\text{C}_6\text{H}_5$. This crystallized from gasoline in fine, white needles melting at 117° . The same urea was also prepared by heating *o*-toluidine and the methyl phenyl urea chloride at 125° .

Calc. for $\text{C}_{14}\text{H}_{16}\text{ON}_2$: N, 11.66%. Found: 11.50%, 11.72%.

Under like conditions, diphenyl urea chloride and the ethyl ether of isothio di-*o*-tolyl urea gave ethyl chloride, *o*-tolyl mustard oil and α, α -diphenyl- β -*o*-tolyl urea, white crystals easily soluble in alcohol, benzene and chloroform, moderately soluble in gasoline, with a melting point of 85° .

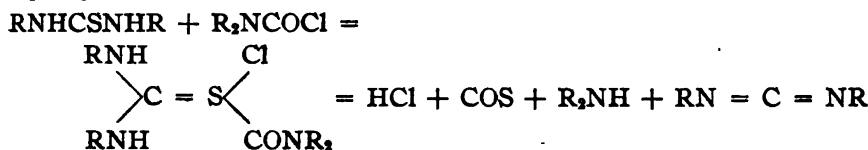
Calc. for $\text{C}_{20}\text{H}_{18}\text{ON}_2$: N, 9.27%. Found: 9.05%, 9.11%.

The mechanism of the reaction between the urea chlorides and the substituted ureas and the thiourea ethers is open to question. Dixon² has suggested that the acyl chlorides react by first addition to the sulfur atom which becomes tetravalent. These addition products which have been isolated in many cases break down, either by heating above their dissociation points or under the influence of solvents, loss of halogen hydride occurs and the acid group of the type RCO migrates to a nitrogen, giving acyl nitrogen derivatives. The stability of the resulting substitution product seems to depend upon the presence of a reactive anilido hydrogen. Thus acetyl-diphenyl thiourea easily dissociates into acetanilide and phenyl mustard oil, while the dibenzoyl diphenyl thiourea is stable. When a phenyl group is replaced by the more positive allyl grouping the ease of decomposition seems to be increased, as will be

¹ *Ber.*, 17, 2593 (1884).

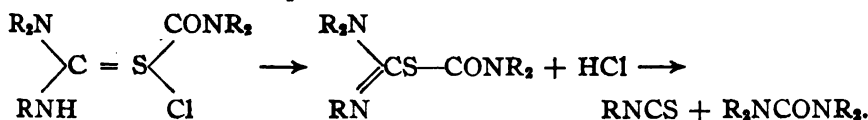
² *J. Chem. Soc.*, 101, 2519 (1912).

noted later. This assumption of first addition to the sulfur atom affords a logical explanation of the action of the urea chlorides. For instance, diphenyl-thiourea and a urea chloride could react as follows:



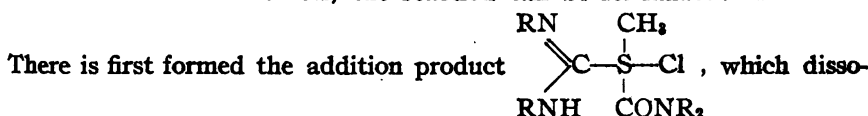
The addition compound breaks down into the simpler products hydrogen chloride, carbonyl sulfide, diphenylamine and carbodiimide.

The carbodiimide now attacks a mol of unchanged thiourea, yielding triphenyl-guanidine and phenyl mustard oil. The explanation agrees wholly with experimental facts. In the case of the trisubstituted thioureas the first addition product would be



Here the absence of hydrogen prevents the formation of diphenylamine and the compounds breaks down into the mustard oil and a tetrasubstituted urea.

With the thiourea ethers, the reaction can be formulated as follows:



ciated into methyl chloride, mustard oil and a trisubstituted oxygen urea.

Allyl Thioureas and Acid Chlorides.—In a previous paper,¹ it was shown that acetyl chloride acting directly without a solvent upon allyl-phenylthiourea converted it easily and smoothly into the isomeric 2-anilido-5-methyl-4,5-dihydrothiazole. Dixon later made the same observation.² We have now found that by modifying the conditions, it is possible to obtain from the allyl thioureas and acyl chlorides, not only the thiazoles but also their acyl derivatives. Molar proportions of allyl-phenylthiourea and pyridine were dissolved in benzene and one mol of benzoyl chloride added to the mixture. After standing, the benzene solution was filtered from the pyridine hydrochloride and the solution washed with dilute acid to remove any excess pyridine. From the benzene on evaporation at room temperature white crystals melting at 125° were obtained, which proved to be α -allyl- β , β -benzoyl-phenylthiourea, $\text{C}_9\text{H}_9\text{NHCS}(\text{COC}_6\text{H}_5)_2$. That the above constitution is correct is shown by the

¹ THIS JOURNAL, 22, 192 (1900).

² J. Chem. Soc., 93, 24 (1908).

fact that when the benzene solution of the allyl-benzoyl-phenyl thiourea is concentrated with the aid of heat, it decomposes quantitatively into allyl mustard oil and benzanilide.

Acetyl chloride was allowed to react with a mixture of allyl phenyl thiourea and pyridine in benzene solution. After removal of the pyridine and pyridine hydrochloride, the solution was allowed to evaporate at room temperature. The only products obtained were allyl mustard oil and acetanilide. The acetyl-phenyl allyl thiourea, which must have been first formed, evidently breaks down with very great ease. With a substituted phenyl group, the acetyl derivative is more stable. Thus acetyl chloride was added to a benzene solution of allyl *p*-bromophenyl thiourea. From the benzene solution was obtained by evaporation the allyl-acetyl-*p*-bromo-phenyl thiourea. This separates in white crystals melting at 86°.

Calc. for $C_{12}H_{13}ON_2BrS$: Br, 24.42%. Found: 24.11%.

Alcoholic potash removes the acetyl group giving the original thiourea. Warming the compound above its melting point for a few minutes causes it to break down into allyl mustard oil and *p*-bromo-acetanilide.

Under similar conditions, acetyl chloride and allyl-*p*-chloro-phenyl-thiourea gave α -allyl- β -acetyl- β -*p*-chloro-phenyl thiourea, white crystals from benzene melting at 84°.

Calc. for $C_{12}H_{11}ON_2ClS$: Cl, 13.50%. Found: 13.21%.

Heated above its melting point, it decomposed into allyl mustard oil and impure *p*-chloro-acetanilide.

It will be noted in the case of these allyl phenyl thioureas, that the acyl group attaches itself to the nitrogen of the more negative anilido rest and not to the more positive C_3H_5N grouping.

This would seem to be in accord with some previous experimental work,¹ where it was found that when an acid chloride was added to a mixture of two different amines, there was formed the hydrochloride of the more positive amine and the acyl derivative of the more negative one. Whether this will hold good in all cases with thioureas of the type $R'NHCSNHR$ must await further investigation.

Allyl Thioureas and Acid Chlorides. Thiazole Synthesis.—It has been mentioned before that allyl phenyl thiourea with acetyl chloride, in the absence of a solvent, rearranged to a thiazole derivative. The same result is attained when the thiourea and benzoyl chloride are heated at water bath temperature for thirty minutes.

2-*p*-Bromophenylamido-5-methyl-4,5-dihydrothiazol.—This is easily made by heating *p*-bromo-phenyl allyl thiourea with acetyl chloride for twenty minutes. The reaction product was dissolved in dilute alcohol

¹ Dains, THIS JOURNAL, 28, 1184 (1906).

and then made alkaline with sodium carbonate solution. The white precipitate after recrystallization from alcohol melted at 107° . It is soluble in the ordinary organic solvents and in acids. Its picrate melts at 156° . The same thiazole was prepared by heating the allyl-*p*-bromophenyl-thiourea and concentrated hydrochloric acid in a pressure flask on the water bath until all the thiourea had gone into solution.

Calc. for $C_{10}H_{11}N_2BrS$: N, 10.40%. Found: 10.70%, 10.63%.

2-*p*-Chloro-phenylamido-5-methyl-4,5-dihydro-thiazole from acetyl chloride and allyl *p*-chloro-phenyl thiourea forms white crystals out of alcohol, melting at 116° .

Calc. for $C_{10}H_{11}N_2ClS$: N, 12.40%. Found: 12.58%.

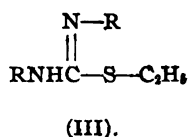
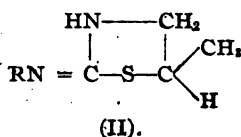
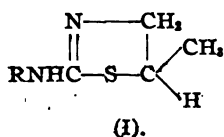
Its hydrochloric acid salt is precipitated when dry hydrogen chloride is passed into the benzene solution of the base. It melts at 226° .

Calc. for $C_{10}H_{11}N_2ClS.HCl$: HCl, 13.86%. Found: 14.20%.

m-Tolylamido-5-methyl-4,5-dihydrothiazol.—Acetyl chloride converts the allyl-*m*-tolyl-thiourea quantitatively into the corresponding thiazole. This recrystallized from alcohol melts at 90° . The picrate melts at 158° . It is readily soluble in alcohol, benzene, gasoline and dilute acids, very soluble in chloroform.

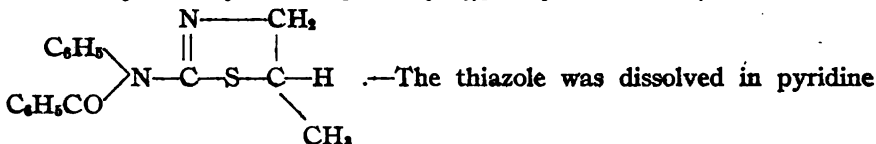
Calc. for $C_{11}H_{14}N_2S$: N, 13.60%. Found: 13.48%, 13.26%.

The Thiazoles and Acid Chloride.—It will be noticed that the thiazoles thus formed bear a close relationship in structure to the isothiurea ethers. Both types of compounds contain an amidine grouping and a sulfur atom linked to two carbons.



Formulas I and II show the tautomeric forms of the same thiazole and III an isothiurea ether with analogous grouping. The anilido hydrogen in the isourea ethers can be easily replaced by an acyl group, and experiment has shown that the corresponding hydrogen in the thiazoles is equally reactive toward acetic anhydride,¹

2-Phenyl-benzoyl-amido-5-methyl-4,5-dihydro-thiazole,



and benzoyl chloride added. From the reaction product was isolated

¹ Young and Crookes, *J. Chem. Soc.*, 89, 65 (1906); Traumann, *Ann.*, 244, 31 (1888).

the above benzoyl derivative. Purified from alcohol it separates in white crystals melting at 118° . It is soluble in ether, readily soluble in carbon bisulfide, alcohol and benzene, very soluble in chloroform.

Calc. for $C_{17}H_{16}ON_2S$: N, 9.46%. Found: 9.65%, 9.74%.

It is isomeric with the allyl-phenyl-benzoyl-thiourea. The thiazole is no longer basic and the benzoyl group is easily split off by either alcoholic potash or cold hydrochloric acid, yielding the original thiazole. There is of course a possibility that the benzoyl group is attached to the nitrogen at 2, but the evidence seems to be in favor of the above formula. Thus Prager¹ and Young and Crookes² have shown that when this thiazole unites with methyl iodide, the methyl group goes to the nitrogen to which the phenyl group is attached and secondly it has been pointed out in this paper that when benzoyl chloride acts on allyl-phenyl-thiourea, the product contains a benzoyl and a phenyl group on the same nitrogen atom.

Further investigation along these lines is being continued in this laboratory.

LAWRENCE, KANSAS.

[CONTRIBUTION FROM THE SYNTHETIC PRODUCTS LABORATORY OF BUREAU OF CHEMISTRY.]

RESEARCHES ON ORGANIC PERIODIDES.

I. PERIODIDES OF PHENACETIN, METHACETIN AND TRIPHENIN.

By W. O. EMERY.

Received November 4, 1915.

Introduction.

The first comprehensive study of organic periodides was inaugurated by Joergensen³ in 1869. Since that time many new periodides as well as other perhalides of both organic and inorganic bases have been prepared and investigated more or less thoroughly from varying viewpoints, notably as regards composition, mechanism of formation and availability for purposes of quantitative analysis.

In connection with a general plan for the systematic development of tests and methods applicable to drug analysis, it was decided to investigate the iodine addition-products or periodides of some of the more important synthetic compounds of a quasi-alkaloidal character, with a view to the eventual use of such products in analytical operations.

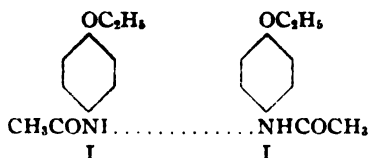
The study of periodides in general, as also those of the phenetidine type in particular, had its inception in the insistent demand for a procedure designed to effect a quantitative separation of phenacetin (acet-phenetidine) and acetanilide in admixture. In searching the literature

¹ *Ber.*, 22, 2990 (1899).

² *J. Chem. Soc.*, 89, 59 (1906).

³ *J. prakt. Chem.*, [2] 2, 433 (1869).

for derivatives which might possibly serve as a basis for the purpose indicated, an iodine derivative of phenacetin was noted, the so-called "jodophenin" of Scholvien and Riedel,¹ a patented preparation alleged to have the composition: $C_{20}H_{25}N_2O_4I_3$, thus in form at least a partial substitution-product, prepared by the action of iodized potassium iodide solution on phenacetin in the presence of a mineral acid and more particularly described by Scholvien,² although Ritsert³ claims to have observed its formation at an earlier date. Among other things, Scholvien found that the compound readily yielded its iodine both to caustic alkali and sodium thiosulfate, and he accordingly employed the latter reagent in a quantitative determination of this element, thereby assuming that the thiosulfate accounted for the total iodine content of the product. The apparent ease with which the iodine could be thus detached forced the conclusion that the interaction of phenacetin with iodine resulted in addition rather than substitution, although the iodine content of 51% as determined by titration seemed to indicate a mixture of equal parts of a mono- and diiodophenacetin. However erroneous the view, Scholvien finally decided that the product, to which he assigned the fanciful name: "jodophenin," was a triiodophenacetin representing a combination of phenacetin and iodine in the proportion of two molecules of the former to three atoms of the latter; that it had the empirical formula: $C_{20}H_{25}N_2O_4I_3$, corresponding to an iodine content of 51.5%; that finally such a compound could possess only the following constitution:



This conception has heretofore apparently been received without question, judging from the attitude of Beilstein⁴ and Piutti⁵ toward the product. Kunckell⁶ indeed goes so far as to regard the substance in the light of a true substitution-product, citing its formation among other instances as an example of the introduction of negative radicals or elements into the aromatic nucleus!

Very early in the present investigation it became quite evident that, while the product of the action of iodized potassium iodide on phenacetin

¹ *Handbuch d. organ. Chem. Ergaenzungsband II*, 1900, p. 401; Friedlaender, *Fortschritte d. Theerfarbenfab. III*, p. 875; Riedel, D. R. P. 58409; *Ber.*, 25, 235, Ref. (1892).

² *Pharm. Zentr.*, 32, 311 (1891).

³ *Ibid.*

⁴ *Lac. cit.*

⁵ *Gass. chim. ital.*, 25, 519 (1895).

⁶ *Ber. pharm. Ges.*, 23, 473 (1913).

in the presence of a mineral acid can under proper manipulation serve as a basis for the quantitative separation of the parent substance from acetanilide in admixture,¹ the composition of the product as given by Scholvien and corroborated by Piutti is nevertheless radically incorrect. Both these chemists proceeded on the erroneous assumption that the only elements entering into combination were phenacetin and iodine, thus entirely ignoring the generally accepted view of the time respecting the composition and mechanism of formation of organic periodides. As a matter of fact, the very formation of such products in general and of the iodine derivative of phenacetin, "jodophenin," in particular is conditioned on the availability not only of the base and iodine, but of hydriodic acid as well, either as such or in form of an iodide and a mineral acid. In other words, when an aqueous, acetic acid or alcoholic solution of phenacetin is treated with a solution of iodine and hydriodic acid, or of iodine, potassium iodide and a mineral acid, substantially in accordance with the method followed by Scholvien, there results a periodide or iodine addition-product, diphenacetin hydriodotetraiodide, having the composition: $C_{20}H_{27}N_2O_4I_5$, or expanded:



with a total iodine content of 63.84%, of which the so-called exterior or additive portion, titratable with sodium thiosulfate, constitutes approximately 51%. The same periodide is also formed on treating the hydriodide:



in acetic acid solution with the calculated quantity of iodine, thus unequivocally establishing the composition of this product as above formulated. In addition to the analytical data presented in the experimental portion of this paper, further evidence confirmatory of the formulae herein given for the iodine and hydriodic acid addition-products of phenacetin is seen in the behavior of the nearly related acetanilide and certain of its derivatives toward the same reagents, as investigated and described by Wheeler and Walden,² and Wheeler, Barnes and Pratt.³ In view therefore of the facts and considerations herein stated, it is certain that Scholvien's "jodophenin" has the composition: $C_{20}H_{27}N_2O_4I_5$, not $C_{20}H_{25}N_2O_4I_3$ as deduced from his analytical results.

A second and lower iodine derivative, but otherwise identical with the tetraiodo addition-product both in form and composition: $C_{20}H_{27}N_2O_4I_4$, or expanded as above:



¹ Emery, *J. Ind. Eng. Chem.*, 6, 665 (1914).

² *Am. Chem. J.*, 17, 612 (1895); 18, 85 (1896).

³ *Ibid.*, 19, 672 (1897).

was likewise isolated from an acetic acid solution of the hydriodide and iodine, but only under exceptional conditions, owing to the fact that in solution it tends to pass into the corresponding higher periodide with consequent separation of free phenacetin.

In studying the action of iodine on imides and substituted imides, notably succinylphenetidine, Piutti¹ took occasion to examine both phenacetin and methacetin (acetanisidine) with respect to their behavior toward iodine and potassium iodide in the presence of hydrochloric acid. So far as the experiments related to phenacetin, Scholvien's interpretation with respect to the composition of the resulting addition-product was accepted *in toto*. Likewise in the case of methacetin, an iodine derivative was obtained to which he assigned the formula: $C_{18}H_{22}N_2O_4I_2$, thus ignoring absolutely the part played by potassium iodide and hydrochloric acid. Piutti, like Scholvien, entirely overlooked the fact that in the formation of the above mentioned products hydriodic acid is as essential a factor as iodine itself. In other words, the composition of the methacetin derivative, whether prepared *via* Piutti or more systematically from iodine and methacetin hydriodide: $(C_9H_{11}NO_2)_2.HI$, in a suitable solvent, invariably has the form $C_{18}H_{22}N_2O_4I_2$, or developed like the corresponding phenacetin compound $(CH_3OC_6H_4NHCOCH_3)_2.HI.I_2$.

A tetraiodo derivative of methacetin, corresponding in form to the higher and more stable of the two periodides of phenacetin, has thus far eluded isolation, although indications of the existence of such a compound have been observed under certain favorable conditions.

With triphenin (propiophenetidine), periodides similar in form to the phenacetin derivatives were prepared



and



which, however, differ therefrom in chemical behavior, in that periodide formation finds more ready expression in the di- than in the tetraiodo compound.

From the foregoing it will be sufficiently clear that all periodides directly involved in the present investigation are assumed to be derivatives of salts made up of a phenetide and hydriodic acid, in the proportion of two molecules of the former to one of the latter. This assumption harmonizes well with the now generally accepted view, namely, that organic periodides are as a rule combinations of bases or base-like substances with a mineral acid and iodine, and is, furthermore, in complete accord with certain very nearly related experiments by Noelting.

¹ *Loc. cit.*

and Weingaertner,¹ as also by Wheeler and associates,² on the salts and halogen addition-products of the anilides. Accordingly, it has seemed proper in a presentation of experimental material to describe first, the hydriodides or salts intermediate to the periodides, and second, the last named substances prepared in the usual way or more systematically perhaps from their hydriodides.

Experimental.

Hydriodides of Phenacetin (Acetphenetidine) and Methacetin (Acetanisidine).—In general, these salts were obtained by treating an anhydrous, alcohol-free ethyl acetate or chloroform solution of the quasi-base with gaseous hydriodic acid previously freed from iodine and moisture by passing over red phosphorus and phosphorus pentoxide in the order named. This reagent may be conveniently generated by warming a mixture of equal parts of iodine, rosin and sand, substantially as described by Kastle and Bullock.³ In order to avoid clogging by the newly formed salt, the delivery tube slightly funneled at the base should just barely touch the surface of the reacting solution. Instead of ethyl acetate, chloroform or a mixture of the two may be employed. Since the resulting products are only very slightly soluble in either menstrum, the yields are quite satisfactory. Reaction manifests itself almost immediately in the deposition of colorless needle-like crystals and is complete in a comparatively short time. For purposes of analysis or subsequent use in periodide synthesis, the crystalline product is quickly transferred by pouring and washing with sufficient fresh solvent, to a small suction plate, and, after standing some hours in the open, placed in a suitable glass-stoppered container. Even in such receptacles, the air-dried crystals gradually acquire a yellowish cast with here and there faint spots of red, indicating superficial oxidation. In perfectly dry air the product is reasonably stable, but immediately yields its acid to water or alcohol if brought into contact with these liquids, in this respect behaving much like the halide salts of caffeine. Accordingly, the determination of iodine in such compounds is readily effected by dissolving the sample in hot water and precipitating with silver nitrate, the resulting silver iodide being filtered and weighed in a gooch in the usual way. All hydriodides of phenetidine derivatives so far isolated are representatives of the 2 : 1 type, *i. e.*, two molecules of the base to one of acid. In the case of triphenin, no hydriodide could be isolated in the pure state. No precipitate is formed on treating an ethyl acetate, chloroform or even benzene solution of triphenin with hydriodic acid. On evaporating the solutions so treated either spontaneously or by the aid

¹ *Ber.*, 18, 1340 (1885).

² *Loc. cit.*

³ *Am. Chem. J.*, 18, 109 (1896).

of a blast and gentle heat, a crystalline residue was obtained consisting of a mixture of nearly colorless needles or prisms with periodide-like crystals. It is highly probable that the lighter colored crystals consist essentially of the hydriodide, since the mixture on treatment with iodine in either acetic or propionic acid solution readily yields a periodide.

Acetphenetidine Hydriodide, $(C_9H_9OC_6H_4NHCOCH_3)_2.HI$.—This salt is easily obtained by treating 3 g. phenacetin dissolved in 25 cc. alcohol-free ethyl acetate with hydriodic acid as above outlined. It forms colorless needles melting at $147-8^\circ$ in a closed capillary. It is readily soluble in alcohol and acetic acid, but is decomposed by water, the resulting phenacetin remaining for the most part undissolved.

Calc. for $(C_{10}H_{11}NO_2)_2.HI$: I, 26.10. Found: I, 26.15.

Acetanisidine Hydriodide, $(CH_3OC_6H_4NHCOCH_3)_2.HI$.—This compound was prepared in substantially the same way as the preceding, by treating 5 g. methacetin dissolved in 20 cc. ethyl acetate with the required amount of hydriodic acid. After removing the solvent by suction, the salt was washed several times with alcohol-free chloroform. The resulting colorless air-dried crystals melted at about $125-7^\circ$ in either an open or closed capillary.

Calc. for $(C_9H_{11}NO_2)_2.HI$: I, 27.69. Found: I, 27.32.

Periodides of Phenacetin (Acetphenetidine), Methacetin (Acetanisidine) and Triphenin (Propiophenetidine).—The preparation of these products was effected by various methods, differing more or less in detail but embodying the following salient features: (1) treatment of the base with iodine, potassium iodide and hydrochloric acid; (2) treatment of the base with iodine and aqueous hydriodic acid of known strength; (3) treatment of the base with iodine and an aqueous-alcoholic hydriodic acid of known strength, obtained by dissolving the requisite amount of potassium iodide in a minimum of water, adding thereto a corresponding amount of concentrated hydrochloric acid followed by sufficient absolute alcohol to precipitate the resulting potassium chloride and then filtering; (4) treatment of the hydriodide of the base, if available, with the required amount of iodine.

The analytical methods observed in determining the iodine content of the periodides were: for total iodine, treatment of the air-dried sample according to Carius, or with sulfur dioxide in aqueous-acetic acid solution followed by precipitation with silver nitrate; for free or "exterior" iodine, titration in alcoholic solution with sodium thiosulfate, the quantity of alcohol ordinarily used for this purpose being 10 cc. for every 200 mg. sample. The hydriodic acid present was estimated by difference.

Acetphenetidine Hydriodo-diiodide, $(C_{10}H_{11}NO_2)_2.HI.I_2$.—It was only after repeated trials that this product could finally be isolated in ap-

parently pure condition. Attempts to prepare it in accordance with procedures substantially as indicated above were successful only with the fourth, the others invariably yielding mixtures of phenacetin and the higher tetraiodide. On dissolving, for example, 6 g. of the hydriodide and 3 g. iodine in 20 cc. hot acetic acid, and allowing the resulting mixture to cool, ruby red to reddish brown needle-like crystals were obtained, which in air-dried condition soften at $120-1^{\circ}$ and melt at $124-5^{\circ}$ in a closed capillary. The product thus prepared is sufficiently pure for analytical purposes, as evidenced in the iodine values obtained. Recrystallization, therefore, is inadvisable, the more so since such treatment is inclined to yield mixtures of the original substance with more or less phenacetin and the higher tetraiodide, thus plainly indicating a preferential formation of the latter product at the expense of the former.

Calc. for $(C_{10}H_{12}NO_2)_2 \cdot HI \cdot I_2$: I_2 , 34.29; I_3 , 51.44; HI , 17.27. Found: I_2 , 34.44; I_3 , 51.90; HI , 17.60.

Acetphenetidine Hydriodo-tetraiodide, $(C_{10}H_{12}NO_2)_2 \cdot HI \cdot I_4$.—This periodide perhaps occupies the most important place in the present investigation. Its peculiar properties constituted one of the principal incentives to the work in hand and now afford a practical basis for effecting the quantitative separation of acetanilide and phenacetin in admixture, a result heretofore impossible of accomplishment owing to the lack of a suitable method. The compound has been prepared by all the methods enumerated above, as also by treating the hydriododiiiodide with the required amount of iodine in a suitable solvent. The usual and most convenient method for its preparation is a modified form of Scholvien's procedure,¹ involving the interaction of phenacetin with either iodine, potassium iodide and hydrochloric acid on the one hand, or with iodized hydriodic acid on the other. The behavior of phenacetin under the former treatment is illuminating. On adding iodized potassium iodide solution, for example, to an aqueous, alcoholic or acetic acid solution of phenacetin, the resulting liquid remains perfectly clear. If, however, a mineral acid like hydrochloric be subsequently added, reddish brown leaflets or steely blue needle-like prisms immediately appear, almost or quite insoluble in the resulting menstrum, depending on the temperature, concentration, nature of solvent media and accompanying salts. A very careful study of the widely varying conditions under which iodine addition-products of phenacetin may be prepared shows conclusively that Scholvien's views with respect to periodide formation in general and to the preparation: "jodophenin" in particular are not alone fallacious, but erroneous as well, since the crude product invariably obtained when operating in accordance with his instructions is a mixture, consisting in large measure apparently of the hydriodo-tetraiodide but containing

¹ *Loc. cit.*

some of the lower diiodide as well as free phenacetin, and possessing an exterior and total iodine content considerably less than the required values for the former compound. Thus, two samples prepared under slightly varying temperature conditions but otherwise *via* Scholvien, by treating a solution of 30 g. phenacetin in 225 g. acetic acid with 45 g. concentrated hydrochloric acid and 150 g. water, followed by a solution of 34 g. iodine in 65 g. potassium iodide and 65 g. water, yielded on analysis the following results:

Calc. for $(C_{10}H_{11}NO_2)_2 \cdot HI \cdot I_2$: I_2 , 34.29; I_2 , 51.44. Found: I_2 , 46.85, 48.78; I_2 , 56.52, 57.06.

Calc. for $(C_{10}H_{11}NO_2)_2 \cdot HI \cdot I_4$: I_4 , 51.07; I_4 , 63.84.

If, on the other hand, the quantity of iodine is increased by about 30%, or to 45 g., the resulting addition-product is uniform and susceptible of isolation in a state of high purity. The procedure is further improved by decreasing the quantity of hydrochloric acid to about 30 g. and adding same to a hot solution of the other ingredients, thereupon allowing the mixture to slowly cool to room temperature. The periodide is conveniently isolated by transferring the crystalline magma to a small suction plate provided with a suitable filter, washing the mass several times with saturated aqueous iodine solution and permitting it to dry in the open on a porous plate. In this condition the crystals melt at $133-4^\circ$, dissolve quite readily in alcohol and acetic acid, less so in benzene, chloroform, dilute acetic acid and water, practically insoluble in moderately concentrated solutions of iodized potassium iodide. Although reasonably stable in the air, protracted exposure of the substance to atmospheric influences eventually induces an appreciable lightening in the color of the crystals, the latter becoming in the course of several months nearly or quite colorless, until finally a residual product remains which while retaining the form of the original crystals consists essentially of phenacetin, as identified by the melting point. The relative ease, with which periodides of this class yield their exterior or added iodine to sulfites, caustic alkalis and sodium thiosulfates, at once suggests a ready method for quantitative operations. The exterior iodine was determined by titration with thiosulfate, usually of twentieth normal strength. The total iodine on the other hand was estimated partly by Carius, or more quickly and as accurately by first treating the substance in acetic acid with a saturated solution of sulfur dioxide in water followed by precipitation with silver nitrate. The determination of carbon and hydrogen was effected only after repeated attempts, on account of unusual difficulties encountered in the fixation of iodine during combustion. Satisfactory results were finally obtained by employing lead chromate in connection with spirals both of reduced and silvered copper. In the estimation of nitrogen, the Kjeldahl method was used. In order to determine the

basic portion of the periodide as such, a 200 mg. sample was treated with a saturated aqueous solution of sulfur dioxide until the iodine was completely reduced, the resulting mixture being thereupon extracted several times with chloroform. On evaporation of the solvent, 0.0725 g. (calc. 0.0721 g.) crystalline residue remained, melting at 134-5° and otherwise possessing all the characteristic properties of phenacetin. In addition to evidence already presented, the following analytical results clearly establish the composition of acetphenetidine hydriodo-tetraiodide as expressed in the accompanying formula:

	Calc. for (C ₉ H ₁₁ NO ₂) ₂ .HI.I ₄ :		Found.				
C.....	24.16	...	24.46	24.40
H.....	2.74	...	2.78	2.92
N.....	2.82	...	2.81	2.81
O.....	6.44
I ₄	51.07	51.25	51.05	51.10	51.20	51.12	...
I ₂	63.84	63.89	63.92	63.74
HI.....	12.87	12.74	12.97	12.74

In the qualitative examination of preparations and mixtures of which phenacetin is a suspected or declared ingredient, the above-described periodide may be made the basis of a very delicate identification test for the parent substance. In a test tube containing 1-2 mg. of the phenacetin in question, previously isolated by extraction with chloroform, add a drop of acetic acid, 0.5 cc. of water and 1 cc. of a tenth normal solution of iodine, warm the mixture to about 40°, then add a drop of concentrated hydrochloric acid. If phenacetin alone is present, the periodide separates almost immediately in form of needle-like prisms or leaflets. In the event that the sample contains some acetanilide, the addition-product may appear as reddish brown leaflets only after cooling and agitating the liquid. In the presence of considerable acetanilide, the periodide first separates in the form of minute oily globules, which on vigorous shaking gradually solidify to crystalline aggregates. This test is sufficiently delicate to detect as little as 0.5 mg. phenacetin, if alone, in the form of its characteristic hydriodo-tetraiodide.

Acetanilidine Hydriodo-diiodide, (C₉H₁₁NO₂)₂.HI.I₂.—This compound was first described by Piutti,¹ who obtained it in the form of reddish brown laminae by treating a hot solution of 30 g. hydrochloric acid (presumably concentrated, since this investigator followed very closely the proportions used by Scholvien in making the phenacetin derivative) in 150 g. of water, and a warm solution of 36 g. iodine and 72 g. potassium iodide in 100 g. of water. The composition as found by Piutti was expressed in the formulae: C₁₈H₂₂N₂O₄I₃ = (C₆H₄^{NHCOCH₃}_{CH₃})₂I₃, or one

¹ *Loc. cit.*

hydrogen less than the number actually required for the hydriodo-diiodide, namely: $C_{18}H_{22}N_2O_4I_2$. Thus, it is seen that this chemist, like Scholvien, failed utterly in recognizing the function of hydriodic acid in periodide formation. On repeating Piutti's work, reddish brown leaflets resulted, which were found to have the composition: $C_{18}H_{22}N_2O_4I_2$. Even when the iodine was reduced one-third, or to 24 g., the theoretical requirement of halogen for the production of the hydriodo-diiodide, the same compound was obtained. Likewise, when the quantity of iodine was increased to 48 g., or sufficient to yield a tetraiodide, the sole resulting addition-product was the diiodide. In fact, neither from methacetin nor from its hydriodide as the starting point has it been found possible thus far to isolate a tetraiodo addition-product, although, as previously pointed out in the introduction, signs are not wanting—notably certain color changes in the crystalline products before and after separation from the mother liquor—to the effect that under favorable conditions a tetraiodide may indeed exist.

Acetanisidine hydriodo-diiodide, melting at $142-3^\circ$, was obtained in several crystalline forms and varying shades of color, as reddish brown leaflets or scales, ruby red prism-like aggregates, and thick garnet colored prismatic plates, depending on temperature, concentration and nature of solvent.

	Calc. for ($C_8H_9NO_2$) $_2$.HI.I $_2$:	Found:				
C.....	30.34	30.42	30.48
H.....	3.25	3.34	3.39
N.....	3.94	3.99	3.90
O.....	8.99
I $_2$	35.64	35.14	35.62	35.35	35.21	35.32
I $_2$	53.46	53.17	53.33	53.40
HI.....	17.96	18.03	17.71	18.05

Propiophenetidine Hydriodo-diiodide, $(C_{11}H_{16}NO_2)_2$.HI.I $_2$.—This product is formed when an aqueous-alcoholic solution of triphenin is treated with iodine and hydriodic acid in varying proportions. The best yield was obtained by dissolving 5 g. of the base in 10 g. hot alcohol, then adding thereto a solution of 3.5 g. iodine in 5 g. hydriodic acid (sp. gr. 1.7) followed by 10 g. warm water, finally allowing the mixture to cool very slowly by immersion in warm water. The resulting greenish bronze, needle-like crystals, after being filtered by suction, washed with a little iodized 50% alcohol and dried in the air, melted in a closed capillary at $121-3^\circ$. An increase in the quantity of hydriodic acid to 7.5 g. and of iodine to 7 g., an amount of halogen theoretically sufficient to yield to tetraiodo addition-product, led to the formation of steely blue crystals, but a product otherwise identical with the above both in composition and melting point. Recrystallization from either acetic or propionic acid

was productive of very fine greenish bronze colored needles. Analysis of the crystals obtained in various ways show them to have the composition of the hydriodo-diiodide.

	Calc. for (C ₁₁ H ₁₅ NO ₂) ₂ .HI.I ₂ :	Found:				
I ₂	33.04	32.84	32.78	32.91	32.99	33.00
I ₂	49.56	49.48	49.45
HI.....	16.65	16.64	16.67

Propiophenetidine Hydriodo-tetraiodide, (C₁₁H₁₅NO₂)₂.HI.I₄.—This compound was obtained in the form of fine purple-black silky needles by dissolving the preceding periodide, together with the calculated quantity of iodine, in a small volume of hot acetic acid and allowing the mixture to cool very slowly. After separation from the mother liquor in the usual way, the crystals melted air-dried and in a closed capillary at 92–4°.

Calc. for (C ₁₁ H ₁₅ NO ₂) ₂ .HI.I ₄	I ₄ 49.67	I ₄ 62.08	HI 12.51
Found.....	49.72	62.35	12.63
	49.70	62.21	12.51

Both this and the diiodide are quite soluble in alcohol and acetic acid, only moderately so however in aqueous dilutions of these solvents.

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THE ROLE OF ATMOSPHERIC OXYGEN IN THE OXIDATION OF GLUCOSE WITH POTASSIUM PERMANGANATE IN THE PRESENCE OF VARYING AMOUNTS OF ALKALI. THE PRODUCTS OF OXIDATION.

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Although it has been known for many years that certain organic substances are capable of complete or partial oxidation in alkaline media through simple exposure to atmospheric air, the extent to which this process may participate in oxidations in alkaline media by means of permanganate, and presumably other oxidizing agents, has not been generally appreciated. The experiments here described show conclusively that maximum participation of atmospheric oxygen in permanganate oxidations occurs with concentrations of alkali corresponding approximately to 0.1 *N* potassium hydroxide. This participation diminishes with alkali concentrations greater or less than this amount. Thus in conducting oxidations with permanganate in the presence of alkali, for the purpose of measuring the quantity of oxidizable organic compound present on the basis of the permanganate consumed, it is as necessary to eliminate the participation of atmospheric oxygen as in any other quantitative oxida-

tion method carried out in the presence of alkali; such for example as in any of the numerous sugar titration procedures.

The fact that this large participation of atmospheric oxygen occurs in oxidations with permanganate in alkaline solution was first noted in some earlier experiments on the complete oxidation of propylene glycol with potassium permanganate in alkaline solution¹. It was found that at times as little as 80% of the calculated amount of permanganate was required for complete oxidation. The literature² indicated that the composition of the manganese oxide precipitate may be quite variable and contain much manganous oxide mixed with the dioxide. Thus it seemed possible that the extra oxidation could have been due to the reduction of the manganese dioxide to manganous oxide. But an analysis of the manganese oxide precipitate showed that the manganese is certainly all present as the dioxide in the alkaline oxidations. It was in this way that the extent of the participation of atmospheric oxygen in the oxidation was determined quantitatively.

Although numerous observations have already been made, which in a general way show that the character of the products obtained by the oxidation of certain organic substances in the presence of alkali (notably sugars) differ with varying concentrations of alkali, the present experiments show with precision the varying quantities of the sole end products (carbon dioxide and oxalic acid) which result from the complete oxidation of glucose by means of potassium permanganate for each initial concentration of alkali used (*i. e.*, between no alkali and 1.8 *N* KOH). It was also found that the relative quantities of carbon dioxide and oxalic acid formed not only vary with the initial concentration of alkali employed but also with the total quantity of alkali available, owing presumably to the fact that the initial alkali concentration falls as oxidation with its coincident acid formation progresses, except in those cases in which the total quantity of alkali added in proportion to the amount of glucose used was so excessive that such a fall in alkali concentration was almost negligible.

Experimental Part.

All the oxidations were carried out by dissolving 2 g. of pure crystalline *D*-glucose in 1000 cc. of water and adding variable amounts of potassium hydroxide as shown in the table. The oxidations were carried out in two series.

Series 1.—Expts. 1 to 8 were carried out by adding the amount of potassium hydroxide indicated in the table for each experiment before adding the permanganate. The permanganate was powdered and weighed (20 g. each) into small bottles, numbered to correspond with the solutions

¹ Evans and Witzemann, *THIS JOURNAL*, 34, 1086 (1912).

² Cf. Gmelin-Kraut-Friedheim, *Hdb. der Anorg. Chem.*, 3, Part 2, p. 254 (1906-8), etc., for references.

to be oxidized. The oxidations were done at room temperature as follows: A small amount of the permanganate was added to each solution. The reaction in each case set in at a rate that was proportional to the concentration of the potassium hydroxide. This was especially true of Expts. 4, 5, 6 and 7. There were marked differences in the character of these precipitates. The difference was evident throughout the experiment and gave qualitative support to the idea that the variation in the amount of alkali causes marked differences in the physical character of the oxide of manganese formed in these reactions. Since Solutions 1, 2 and 3 did not become clear, *i. e.*, the manganese dioxide did not settle out, it was at first thought that oxidation was not taking place. Even after standing a month, or more, these red-brown solutions did not clear in the customary way. However, it was discovered that they could be further oxidized and the experiments were continued. As was learned later, these red-brown liquids were due to manganese dioxide in colloidal form.¹ Toward the end of the experiment these colloidal solutions were gradually precipitated as the concentration of the salts (mostly carbonates) increased.

After each addition of permanganate the mixture was agitated from time to time until the portion added was reduced. Permanganate was added in this way until the last portion was only reduced after standing several days and after frequent agitation. In a few cases in which an excess of permanganate had been added 1 cc. portions of 1% glucose solution were added from time to time, until reduction was complete. The unused permanganate in the original weighed portions was weighed and subtracted from the amount taken in the beginning. This gave in each case the amount of permanganate actually used (data given in Col. II in the table). Several weeks were required to complete the oxidations in this way.

Qualitative tests failed to reveal other products of oxidation than carbon dioxide and oxalic acid. Tests for acetic and formic acids and for substances reducing to Fehling's solution were negative in all experiments.

Series 2.—The second series (Expts. 9 to 15) of oxidations was carried out, in part, in order to verify the results of the first series and also in order to determine a little more accurately the conditions under which oxalic acid begins to be formed.

Analysis.

The total carbon dioxide in each experiment was determined by the method previously described² and the amount of carbon dioxide in the potassium hydroxide used was subtracted. This gave the total carbon dioxide formed in any experiment, plus any carbon dioxide that was absorbed from the air.

¹ THIS JOURNAL, 37, 1079-91 (1915).

² *Loc. cit.*

The oxalic acid in 50 cc. of the solution was precipitated as calcium oxalate in a boiling solution acid with acetic acid, by adding boiling calcium chloride solution. The precipitated oxalate was filtered off, washed, dissolved in sulfuric acid and titrated with potassium permanganate in the customary manner. In Expt. 13 a larger amount of the solution was required.

The analysis of the manganese dioxide precipitate offered certain difficulties. Owing to the fact that a considerable fraction of the precipitate is deposited as a mirror on the inside wall of the bottle and cannot be completely removed without dissolving it, an aliquot portion of the precipitate could not be used in the analysis. The following procedure gave little or no difficulty: After the analysis of the solution was complete or after sufficient for the analysis had been pipetted off¹ the precipitate was filtered off in a Büchner funnel in which a wet filter had been arranged so that the edge of the paper extended above the rim of the funnel. This large wet filter was thus folded into a rude filter cup, the wrinkled surfaces of which were pressed down to the surface of the Büchner. A filter of the proper size was previously placed in the funnel in order to support the paper filter cup. The precipitate was all transferred to the funnel and filtration and washing were carried out under suction. The bottle was frequently rinsed in order to wash out all oxalates, especially. The precipitate in the case of the strongly alkaline solutions was washed until it no longer gave a reaction to litmus. The other precipitates were likewise washed in the same way. The precipitate and filter papers were transferred to a large flask, 100 cc. of an oxalic acid solution (1 cc. equivalent to 0.05045 g. KMnO_4) were measured out carefully and part was added to the bottle and the remainder to the precipitate. Dilute sulfuric acid was added to both. The bottle was manipulated until all the manganese dioxide deposited on the glass was dissolved, and the contents were then added to the main portion. When all of the brown precipitate had been dissolved by warming (occasionally 20 cc. more of the oxalic acid solution had to be added) the solution was filtered, the filter washed and the filtrate diluted to one liter. An aliquot portion of the filtrate was titrated for oxalic acid in the usual way. For example, in Expt. 1, 100 cc. of the filtrate required 32.03 cc. of a potassium permanganate solution containing 0.002765 per cc., which corresponds to 0.8856 g. potassium permanganate for the entire filtrate. Therefore 5.045 g. (the potassium permanganate equivalent of the oxalic acid added) minus 0.8856 g. (the potassium permanganate equivalent of the oxalic acid not oxidized by the manganese dioxide) gives 4.16 g. as the potassium permanganate equivalent of the manganese dioxide sludge.

¹ Under vacuum filtration these solutions frequently lose part of the carbon dioxide.

The individual data on the analytical determinations would not be of general interest and so will not be given. The final results in each case are given in the proper place in the table.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
	G.	G.	G.	MnO ₂	MnO ₂	G.	KMnO ₄ deficit		
No.	glucose.	KMnO ₄ used.	KMnO ₄ calc.	equiv. in g. KMnO ₄ .	equiv. calc.	MnO ₂ calc.	from KMnO ₄ .	from MnO ₂ equiv.	Mola. KOH.
8	2.06	13.65	14.46	5.21	5.46	7.51	0.81 g.	0.25 g.	0
9	2.00	13.52	14.04	5.35	5.41	7.43	0.52	0.06	0
10	2.00	13.55	14.04	5.32	5.42	7.45	0.49	0.10	0
11	2.00	12.44	14.04	4.78	4.89	6.84	1.60	0.11	0.5
1	2.00	11.20	14.04	4.16	4.48	6.16	2.85	0.32	1.0
12	2.00	11.48	Expt. was lost		1.0
13	2.00	11.16	14.01	4.29	4.46	6.13	2.85	0.17	1.5
2	2.00	10.35	13.89	4.09	4.14	5.69	3.54	0.05	2.0
14	2.00	10.44	13.69	4.00	4.18	5.74	3.24	0.18	2.0
15	2.00	10.91	13.04	4.39	4.36	6.00	2.13	0	2.5
3	2.00	8.80	12.84	3.42	3.42	4.84	4.04	0	4.0
4	2.04	11.55	12.94	Lost		6.35	1.39	0	8.0
5	2.03	11.30	12.62	4.50	4.52	6.21	1.32	0.02	16.0
6	2.02	11.01	12.62	4.39	4.40	6.05	1.61	0.01	32.0
7	2.02	11.15	12.69	4.40	4.46	6.13	1.54	0.06	64.0

	X.	XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.
No.	G. KOH.	N KOH.	G. CO ₂ .	G. oxalic.	% CO ₂ .	% oxalic.	% re-covered.	KOH for K ₂ salts.	KOH from KMnO ₄ .	Total KOH.	KOH in ppt.
8	0	0	2.99	0	100	0	100	7.61	4.83	3.60	1.23
9	0	0	2.96	0	100	0	100	7.61	4.77	3.57	1.20
10	0	0	2.96	0	100	0	100	7.61	4.79	3.58	1.21
11	0.8	0.014	2.96	0	100	0	100	7.61	4.40	4.12	1.08
1	1.6	0.028	3.04	0	102	0	102	7.71	3.96	4.58	0.98
12	1.6	0.028
13	2.4	0.042	2.89	0.060	98.3	2.00	100.3	7.52	3.95	5.38	0.97
2	3.2	0.056	2.62	0.378	88.6	12.6	101.2	7.20	3.66	5.95	0.91
14	3.2	0.056	2.62	0.356	88.6	11.86	100.46	7.17	3.69	5.96	0.93
15	4.0	0.071	2.23	0.851	74.2	28.3	102.5	6.78	3.86	6.90	0.96
3	6.4	0.114	1.896	1.08	64.12	36.0	101.1	6.22	3.11	8.74	0.77
4	12.8	0.228	2.27	1.044	75.1	34.1	109.2	7.12	4.08	15.89	1.01
5	25.6	0.456	2.046	1.224	69.1	40.26	109.36	6.77	3.99	28.60	0.99
6	51.2	0.912	1.824	1.224	61.6	40.25	101.85	6.20	3.86	54.99	0.97
7	102.4	1.82	1.824	1.274	61.2	42.18	103.3	6.25	3.95	105.4	0.97

Discussion of the Results.

Quite a number of new observations were made in this series of experiments, which have little relation to each other. They will therefore be discussed without any special attempt to interrelate them.

Potassium Permanganate.—The immediate purpose of these experiments was to investigate the amount of potassium permanganate utilized in organic oxidations. The amount of permanganate necessary to completely oxidize the 2.00 g. of glucose in one liter of water in the presence

of the amount of alkali given in Col. X is shown in Col. II. From the data on the sole products of oxidation, recorded in Cols. XII and XIII, the amount of permanganate that would theoretically be required to give these products was calculated as follows: To oxidize 2 g. $C_6H_{12}O_6$ to $3H_2C_2O_4$ requires 9 atoms of oxygen. If 2 molecules of $KMnO_4$ react in alkaline solution to give 3 atoms of oxygen it would require 10.52 g. $KMnO_4$ to oxidize the 2 g. of glucose completely to oxalic acid. In Expt. 13, 2% of oxalic acid was formed. Therefore $10.52 \times 0.02 = 0.21$ g., or the amount of $KMnO_4$ required to give this much oxalic acid. In oxidizing 2 g. of glucose completely to CO_2 , 12 atoms of oxygen are required, and this corresponds to 14.04 g. $KMnO_4$. Since in Expt. 13 98.3% CO_2 were formed, $14.04 \text{ g.} \times 0.983 = 13.80$ g. $KMnO_4$. $13.80 + 0.21 \text{ g.} = 14.01$ g. $KMnO_4$ or the total amount of $KMnO_4$ required to oxidize 2 g. glucose to the products obtained in Expt. 13. All of the others were calculated in the same way. The data are given in Col. III.¹

By comparing the figures in Cols. II and III, it is seen that there is a deficit in the amount of permanganate actually utilized as compared with that calculated from the products of the reaction. It is also seen that this deficit increases as the alkali content is further increased. Thus the deficit previously observed in the oxidation of propylene glycol² was verified by the observations made in the case of glucose. In this case too the largest deficits occurred when alkali was present.

It might appear from these results therefore that oxidations with permanganate in alkaline solutions may result in the liberation of more than 3 equivalents of oxygen from one molecule of permanganate. In order to determine to what extent this hypothesis was tenable the amount of available oxygen in the manganese dioxide sludge in each experiment was determined. This was done in the manner described in the section on analytical methods.

The number of grams of permanganate to which the oxidizing power of the manganese dioxide sludge is equivalent is given in Col. IV. The calculated equivalents, obtained by multiplying the number of grams of permanganate used (Col. II) by $\frac{2}{5}$, are given in Col. V. The permanganate deficits as obtained by subtracting the values in Col. IV from those in Col. V are given in Col. VIII. These data do not in any wise tend to run parallel with the deficit obtained from the permanganate used as given in Col. VII. It has thus been definitely proved that the excess oxidation taking place in these solutions is not indicated by the final condition of the manganese dioxide precipitate.

¹ It is naturally not assumed that a molecule of glucose is ever oxidized *in toto* to 3 molecules of oxalic acid. The calculation was made in this way solely for the sake of simplicity.

² *Loc. cit.*

If, however, the deficit given in Col. VIII is compared with the figures given in Col. XVII, which represent the total amount of potassium hydroxide necessary to convert all of the carbonic and oxalic acids present into their normal salts, and those in Col. XIX, which represents the total amount of alkali derivable from the hydrolysis of the permanganate used, plus the potassium hydroxide used, it is seen that the small deficit observed disappears almost completely when the total alkali present exceeds that necessary for the formation of normal salts. So that as far as these experiments go, there is no evidence for the idea that permanganate is reduced to manganous oxide in any but faintly alkaline solutions.

The observations in the case of neutral solutions are well supported by the exhaustive experiments of Smolka¹ on the oxidation of glucose in neutral solution, (*i. e.*, in the absence of alkalis), under a variety of conditions. These are apparently the only experiments in the literature in which the fate of the permanganate as well as that of the glucose has been followed quantitatively. Smolka oxidized 1 g. of glucose in boiling solution with potassium permanganate added in small portions until the solution remained permanently "red." 1 g. glucose required 6.920 g. KMnO_4 in order to be oxidized completely to carbon dioxide. For 2 g. glucose the KMnO_4 used would be 13.84 g., as compared with an average of 13.55 g. obtained in my own experiments carried out at room temperature. Smolka found 1.31% manganous oxide in his precipitate, which compares favorably with the average deficit of 2.5% observed in my own experiments conducted at room temperature. Smolka attempted to explain away both the permanganate deficit and the manganous oxide found as being largely due to experimental error. From my own experiments it would seem reasonable to expect that the experimental error would be about equal for the whole series. Since this obviously was not observed it must be concluded that there is actually some manganous oxide formed, but only in variable and small percentages when the oxidation is conducted in the manner described above.

The data in Col. VII show that the small deficit in the permanganate used increases rapidly when 0.5 molecule potassium hydroxide is present and apparently arrives at a maximum with 4 molecules of potassium hydroxide, or when the solution is 0.114 *N* alkali to begin with. From the figures in Cols. XVII and XIX it is seen that the solution must contain at least 2.52 g. free potassium hydroxide at the end of the experiment, *i. e.*, about 0.05 *N* alkali. With higher concentrations the deficit drops markedly. The fact that this effect is rather constant for similar conditions is shown by a comparison of the results of the two series, but especially by a comparison of Expts. 2 and 14. The unaccountable variations in

¹ *Sitzungber. d. Math. Naturwissenschaftlichen Klasse d. Kais. Akad. Wissenschaften Wien.*, 95, II, 5-30 (1887).

such experiments are illustrated by Expt. 15. In this case the permanganate deficit should have been more than 3 g. but was actually only 2.13 g. Smolka also found similar variations when using neutral solutions. These variations no doubt depend on slight but imperceptible variations in the technique.

There are three possible explanations of this permanganate deficit in alkaline solutions:

(1) A large proportion of the manganese dioxide is reduced to a manganous compound and subsequently oxidized by the air to manganese dioxide.

(2) The alkali serves as a catalyst in facilitating the oxidation of the glucose and the products of its reaction with alkali, by means of the oxygen of the air. The manganous compounds may have a role in this catalysis.

(3) The combined effect of (1) and (2).

There are no data in the literature that would entitle us to ascribe so large an effect to the first hypothesis.

On the contrary there is much evidence for the truth of the second hypothesis. The extensive work of Nef¹ and his pupils and others, on the incomplete oxidation of sugars and allied compounds, lends strong support to this hypothesis. Perhaps the most directly helpful experiments along this line are those of A. P. Mathews.² Sugar solutions containing various concentrations of alkali were placed in a closed system filled with oxygen. The diminution of oxygen pressure was measured on a manometer in the system. In this way sharp qualitative evidence of the marked effect of small alkali concentrations in producing a relatively enormous increase of the absorption of an oxygen atmosphere by sugar solutions was obtained. Accordingly, if arguments based on analogy in this way have any weight, this hypothesis seems the most probable.

It may be that the true explanation will involve both (1) and (2) as suggested in (3).

The elucidation of the mechanism of this excess oxidation will be of great theoretical interest, but in some ways the fact that it takes place at all, and more especially, the fact that it is so markedly induced by very small concentrations of alkali (even 0.014 *N* alkali gives a strong effect) and that it comes to a maximum at a low alkali concentration (about 0.1 *N*) is of greater practical interest.³ In changing

¹ *Ann.*, 357, 214 (1907); 376, 1 (1910); 403, 204 (1914).

² *J. Biol. Chem.*, 6, 3-20 (1909).

³ Mathews suggests that with glucose the maximum alkali effect was obtained at 0.2 *N*. According to my own experiments atmospheric oxidation was considerably less at 0.228 *N* than at 0.114 *N*, but this may be due in part to the fact that the addition of permanganate to Expts. 1, 2 and 3 was delayed at first, as stated above, owing to the fact that manganese dioxide was not precipitated at the beginning. On the other hand Mathews did not exclude the effect of the increasing solubility of oxygen in alkali solutions. The maximum, however, probably lies close to, or between, 0.1 or 0.2 *N* alkali. It is probable that the total available alkali is of great importance.

from no free alkali to a concentration of 0.114 *N* at the beginning and of 0.05 *N* at the end the maximum alkali effect has been obtained. The fact that minute concentrations of alkali influence many reactions very markedly has long been known, especially to the organic chemist, but such a relatively large and graded effect of small concentrations on organic oxidations, especially when such a powerful oxidizing agent as permanganate has been used, came as a surprise. The fact that this effect has been observed in three independent series of experiments on two different organic compounds (propylene glycol and glucose), and by Mathews working by another method, indicates clearly that these results are not anomalous. There are preliminary data already at hand which indicate that the alkali effect described is not found with all organic compounds and to a variable extent with others. If this proves true we now have a method of quantitatively studying these phenomena.

Products of the Oxidation.—The determination of the products of oxidation in this series of experiments was a secondary object. Smolka found that when glucose is completely oxidized with excess permanganate that the sole product is carbon dioxide. In one instance he found a trace of oxalic acid. In Expts. 8, 9 and 10 the calculated quantity of carbon dioxide was obtained, *i. e.*, 100%. In Expt. 11 0.5 molecule potassium hydroxide was used but the product was the same, likewise, in Expt. 1 in which one molecule of alkali was used. But in 13 with 1.5 molecules of alkali 0.60 g., or 2%, of oxalic acid was found. When the alkali was increased to 2 molecules, or 0.8 g. more alkali was used, the oxalic acid increased to 0.378 g. or 12.6%. The same result was obtained in number 14. From this point on the amount of oxalic acid increases, rapidly at first and then slowly to 1.274 g., or 42.18%, at 64 molecules of potassium hydroxide. Simultaneously there is always a corresponding fall in the carbon dioxide, so that the sum of the products in each case is equal¹ to 100% (cf. Cols. XII, XIII, XIV, XV, and XVII).

One of the most interesting facts brought out is the increase of the oxalic acid production from 2% to 12.6% on adding 0.8 g. additional potassium hydroxide. In seeking an explanation of this fact the calculations recorded in Cols. XVII, XVIII, XIX and XX were made. Col. XVII shows the number of grams of potassium hydroxide necessary to neutralize the carbon dioxide and oxalic acid to their normal salts. Col. XVIII shows the amount of potassium hydroxide that could arise from the permanganate, provided it is completely hydrolyzed. According to Morawski and Stingl²

¹ The variations above 100% are due to the absorption of carbon dioxide from the air. In Expts. 4 and 5, in which the stoppers were subsequently found to have been defective, this error in the CO₂ rises to a maximum.

² *J. prakt. Chem.*, [2] 18, 86 (1878); *Jahresber.*, 1878, 275; cf. also Smolka, *Loc. cit.*, and Gmelin-Kraut-Friedheim, *Handbuch d. Anorg. Chem.*, 3, II, 254, etc.

the precipitate in these experiments is $\text{KH}_2\text{Mn}_4\text{O}_{10}$ plus or minus small amounts of impurities. If we accept this statement as probably true in most of the experiments, the precipitate will contain part of the theoretically available alkali. The potassium hydroxide that could be used in this way was calculated from the data in Col. VI and is given in Col. XX. The figures in Col. XIX, which represent the amount of potassium hydroxide that should be available for neutralizing the carbonic and oxalic acids formed, are obtained by subtracting the values in Col. XX from the sum of those in X and XVIII.

From the figures in XVII and XIX it is seen that the alkali available becomes equal to the alkali required for normal salts in Expt. 15 and that under these conditions we get a maximum yield of oxalic acid. So that in this case the effect of the alkali in increasing the yield of oxalic acid is that it converts more and more of the acids formed into their normal salts and incidentally uses up the free alkali in the process. Now it happens that, of the dibasic aliphatic acids, oxalic acid is the only one known that is not attacked by permanganate in alkaline solution, so that as soon as enough alkali has been added to convert part of the oxalic acid into its normal salt that part becomes unavailable for oxidation if the conditions remain unchanged.

In oxidizing glucose with insufficient permanganate, Smolka found that one molecule of glucose gives one molecule of oxalic acid and four molecules of carbon dioxide, in the absence of alkali. When more permanganate was added the oxalic acid diminished until six molecules of carbon dioxide and no oxalic acid were obtained. The above experiments show that the latter conditions hold true when extra alkali is added, up to the point at which the amount of free alkali becomes equal to or in excess of that required to convert the products into their normal salts.

In calculating the percentage yield of oxalic acid it was assumed, in order to make the products recovered total 100%, that all the carbon is oxidized to oxalic acid, *i. e.*, three molecules of oxalic acid from each molecule of glucose. If, however, the above data of Smolka hold true in all cases, but one molecule of oxalic acid would be formed, *i. e.*, the maximum attainable yield would be 33% oxalic acid. The data show that this is not the true maximum. Furthermore, W. Greifenhagen, J. König, and A. Scholl¹ found on oxidizing various hexoses (0.20 g.), including glucose, in 40 cc. of boiling 20% potassium hydroxide with 50 cc. 0.1 *N* KMnO_4 , that 2 molecules of oxalic acid and 2 molecules of carbon dioxide are formed, *i. e.*, 66% oxalic acid. Their quantitative data correspond very closely with this statement.

It is well known that glucose, as well as other sugars, undergoes marked changes in the presence of alkali and in the absence of oxygen, by which

¹ *Biochem. Z.*, 35, 168-93 (1911).

they are finally broken up into shorter chains which often rearrange, in part at least, into stable compounds such as lactic acid. Moreover, such shorter chain carbon derivatives tend to give quantitatively one molecule of oxalic acid and one of carbon dioxide with permanganate in strongly alkaline solutions.¹ So that although Greifenhagen, *et al.*, obtained about 66% of oxalic acid they were working under conditions in which the maximum decomposing effect of the alkali could be obtained, and therefore the maximum number of short chain molecules. In my own experiments, conducted at room temperature and with much smaller alkali concentrations, the decomposition of the glucose into molecules with shorter carbon chains would be relatively very much smaller. It is therefore clear that Smolka's formulation of the products of the oxidation holds only for the conditions under which he worked. As soon as excess alkali is present in the reaction solutions the signs of the decomposing action of the alkali would be preserved, since oxalic acid is stable under these conditions and since each shorter molecule tends to produce a molecule of oxalic acid. So that roughly, as far as we now know, the amount of oxalic acid in excess of 33% in these cases in which excess alkali was present may be taken as a measure of the amount of this decomposition.²

An additional bit of evidence for this interpretation was obtained thus: Expt. 3 was repeated. 2 g. glucose were dissolved in 1 liter of water and 6.40 g. potassium hydroxide were added to the colorless solution. The mixture was placed on the steam bath for $\frac{3}{4}$ hour and became rich brown in color and had an odor of caramel. After cooling it was treated with solid potassium permanganate a little at a time as usual. 8.52 g. potassium permanganate were required for complete oxidation. 1.255 g. oxalic acid were formed, or 41.83% of that theoretically possible if all the carbon in the glucose were converted into oxalic acid. Only 36% oxalic acid was obtained in Expt. 3. Thus it was shown that even warming a short time before oxidation markedly affects the yield of oxalic acid.

Resume.

It had previously been found in oxidizing propylene glycol with potassium permanganate in alkaline solution that only about three-fourths of the calculated amount of permanganate was utilized in some cases. A special series of experiments on the complete oxidation of glucose with permanganate, in the presence of variable amounts of alkali showed that this deficit in the amount of permanganate required occurs to a slight ex-

¹ The three carbon compounds do not always, as was shown by Evans and Witzemann (*Loc. cit.*), quantitatively give one molecule of oxalic acid plus one molecule of carbon dioxide, in alkaline solution, but the statement is approximately true.

² Greifenhagen, *et al.*, have used a different interpretation which apparently holds true for the 6 carbon compounds but which breaks down with the 5, 4, 3 and 2 carbon compounds with which they also worked.

tent even in the absence of alkali, but increases rapidly on the addition of small amounts of alkali up to a concentration of about 0.1 *N*, after which it diminishes somewhat. By careful analyses of the manganese precipitate, it was found, in the solutions containing little or no alkali, that the oxidizing power of the precipitate was only slightly less than it would have been if all the permanganate used had been quantitatively converted into manganese dioxide. In the more alkaline experiments there was no deficit of this kind. It was thus shown that the excess oxidation in these experiments was not due to a permanent reduction of permanganate to manganous oxide. If it is thus reduced at first it was subsequently oxidized by atmospheric oxygen or permanganate to the peroxide. It is thought probable, however, that a considerable part of the permanganate deficit is due to the direct oxidation of the sugar in the alkaline solution by atmospheric oxygen. Both of the preceding processes may, however, play a part in producing the permanganate deficit. But, whatever the mechanism of this excess oxidation may be, it was clearly demonstrated that the excess oxidation was due to the action of atmospheric oxygen in some way.

The sole products of the complete oxidation of glucose under these conditions are carbon dioxide and oxalic acid. It was shown that the oxalic acid increases very rapidly from none to a large amount within small range of change in alkalinity. But it was successfully proved from the data that this is not solely a question of the initial concentration of the alkali, but is also dependent on the degree to which the initial concentration is maintained. Oxalic acid or potassium acid oxalate are not stable in permanganate solution, so that such oxalic acid as is formed cannot persist even in part until the amount of alkali present is sufficient to convert it into normal potassium oxalate (which is stable in permanganate solution).

Some deductions about the mechanism of the formation of oxalic acid were also made.

CHICAGO, ILL.

NEW BOOKS.

Chemical German. By FRANCIS C. PHILLIPS, Professor of Chemistry in the University of Pittsburg. Second Edition. Pp. viii + 250. Easton, Penna.: The Chemical Publishing Co. Price, \$2.00.

The sub-title of the book expresses its scope. It is "an introduction to the study of German Chemical Literature, including rules of nomenclature, exercises for practice, and a collection of extracts from the writings of German chemists and other scientists, and a vocabulary of German chemical terms and others used in technical literature." The book is intended for students who have had at least a year of German, and who

have mastered the elements of chemistry. It covers the field of inorganic and organic chemistry, and emphasis is put upon the processes used in the laboratory. Selections from the writings of chemists follow the general exercises, the purpose of which is to make the student familiar with the technical vocabulary of the science. These selections are well chosen, both from the standpoint of the language and of the general interest connected with their contents. The student has an opportunity to read from the writings of Wöhler, Berzelius, Döbereimer, V. Meyer and Jacobson, Engler, Elbs, v. Brunck, Bleier, Bunsen, Caro, Jahn, Landolt, and other well known chemists. The vocabulary is excellent; it contains many technical words and abbreviations which can be found elsewhere with difficulty, and it is, therefore, of value to the student who is beginning to read the German chemical journals. The work has been well done and the book merits the success it has reached. In the opinion of the reviewer it is by far the best book published for the student who desires to acquire a reading knowledge of chemical German. The value of the book would be increased by including a few articles on physical chemistry, which introduce the special words used in this branch of the science; or these words could be added to the vocabulary in a later edition.

JAMES F. NORRIS.

Scientific and Applied Pharmacognosy. By HENRY KRAEMER, Professor of Botany and Pharmacognosy, Philadelphia College of Pharmacy. Pp. 857; plates, 300+, comprising about 1000 figs. Philadelphia: M. G. Smith, 145 N. 10th St. Price, \$5.00.

Disputes as to the genuineness and quality of drugs offered for importation into the United States have as frequently been appealed to the chemist as to the botanist, and not infrequently both have been called upon to arbitrate between the importer and the port officials. This work of identification and verification of drugs at ports of entry has created a demand for trained pharmacognosists, a demand which will most likely be increased with the appearance of the new pharmacopoeia, which, for the first time, will devote considerable space to descriptions of the microscopic appearance of vegetable drugs in powdered form.

While employment in the field of applied pharmacognosy has become abundant, the workers are still few in number, and in many cases their training has been along the separate lines of the chemist or botanist, so that they are often called upon to search for information in special fields with which they are not familiar. Most of the available authoritative works on pharmacognosy have been by foreign authors, and give but scant attention to many important plant drugs of American origin; or the information desired has been widely scattered through special journals and not readily accessible to the average worker.

No one was better fitted to fill this gap in the literature of crude drugs

than Professor Kraemer, and this new volume fills it in an eminently acceptable manner.

The volume embraces as comprehensive a survey of the general subject of pharmacognosy as could be looked for within a work of its size, and the subject matter has been assembled and arranged by one who is not only a practical laboratory worker but who has also made numerous valuable contributions to the science. The various drugs are assembled under their respective families, which is not only the most logical arrangement from the standpoint of systematic botany, but facilitates their comparison with allied drug products.

One feature which will be appreciated by the pharmaceutical chemist who is an occasional rather than a constant worker in pharmacognosy are the references to leading articles in other publications which are attached to the description of nearly every important drug. This information will be especially useful to those whose training has been mainly along chemical lines, and is a feature that may with benefit be still further expanded in future editions..

The illustrations are numerous and well executed, most of them from original drawings or photographs by the author, and as a rule are not mere idle embellishments, but have a close and organic connection with the text. But few important drugs have been overlooked in the illustrations, and in many instances, figures of crystalline chemical constituents are given as well as those of tissues and tissue elements.

The concluding section of the volume consists of an elaborate "key" or scheme for the identification of powdered drugs by means of their physical appearance to the eye or under the microscope, which should do much to relieve the feeling of utter helplessness with which the analyst is apt to be afflicted when confronted with a comminuted vegetable drug of unfamiliar organoleptic qualities, and devoid of characteristic chemical constituents which might throw light upon its identity.

This key is almost or quite wholly the original work of the author, and its presence is of itself a sufficient reason for the inclusion of the volume in the library of anyone who has much to do with the identification or testing of powdered vegetable drugs.

J. H. BEAL.

Alcoholometric Tables. By SIR EDWARD THORPE. London: Longmans, Green & Co. 1915. 16 mo., xv + 91 pp. Price, \$1.10, net.

These tables have been compiled under the direction of the long-time principal of the British government laboratory. They were originally published in "A Dictionary of Applied Chemistry," and have now been extended so that Table I shows the percentage by weight and by volume as well as the percentage of fiscal proof spirits for each even number from 0.7940 to 0.9998, or 1030 entries of specific gravity in air at 60° F./60° F.

The greatest difference between consecutive percentages of alcohol is 0.19, so that interpolation is sufficiently easy.

Table II shows for each fifth of a degree of Sikes hydrometer (550 entries) the amount of British proof spirit, of American proof spirit, of alcohol by weight according to the German system of alcoholometry, and of alcohol by volume according to the system adopted in France and according to Tralles.

Table III gives the indications of the hydrometers legalized in Russia, Holland, Spain and Switzerland which correspond to integral degrees of Sikes.

The tables are founded on the results of Mendeléef. The data obtained by Blagden and Gilpin about 1794 and by Drinkwater about 1848, at least those relating to weak alcoholic mixtures, were so good that many of them were included by Mendeléef in his published tables, and the results of these four authorities are the basis of the present convenient and well printed tables.

EDWARD W. MORLEY.

Practical Organic and Biochemistry. By R. H. A. PLIMMER. London: Longmans, Green & Company. Price, \$3.60.

A new improved and extended edition of the author's "Practical Physiological Chemistry," intended primarily for the use of medical students.

Although an attempt has been made to include the latest discoveries in organic and biochemistry, the value of the work as a text-book is largely curtailed by the almost complete absence of theoretical discussion, and, as a reference work, by the necessary omission of many important methods and facts, if the book were to be kept within the bounds to which the author limits himself. However, the work has many good features and would be of great use as a review of the subjects.

Too brief a treatment of important principles leads only to confusion and as one of many such instances may be mentioned that in the chapter on carbohydrates the usual projection formulas for the sugars are given without proof of their configuration.

Unfortunately, there are numerous errors and misstatements. As in the above mentioned chapter, page 174, "Hexahydric alcohols exist in ten stereoisomeric forms;" page 185, "Xylose is obtained from straw and various forms of cellulose. It is optically inactive;" page 195, "Pentoses are dextro-rotatory or inactive." There is a typographical error on page 139 in the formula for azoxybenzene, also an hydroxyl group is omitted in the formula for morphine, page 357, and, page 358, that of narceine contains a carbonyl in place of a methoxy group.

In the chapter on nucleic acids, page 301, inosinic acid is stated to contain xanthine and to be identical with vernine. Many more, less conspicuous errors are present throughout the book.

The best features of the biochemical section are the chapters dealing

with proteins and enzyme action and the analysis of tissue and excretions.

Tables and a list of common reagents are appended.

F. B. LA FORGE.

Chemical Constitution and Physiological Action. By PROF. DR. LEOPOLD SPIEGEL, Berlin. Translated, with additions, from the German by C. LUDERKING, PH.D., Leipsic, and A. C. BOYLSTON, A.M., Harvard. New York: D. Van Nostrand Co. v and 155 p. Price, \$1.25, net.

This concise and able treatise is a translation of an address published originally in the "Sammlung Chemischer und Chemisch-technischer Vorträge," Vol. 14, Enke, Stuttgart. It is obvious that a small work of this type cannot cover with any great thoroughness a vast field bristling with indefinite statements and contradictions which render extremely difficult the culling of the main facts and principles. The author has, however, succeeded admirably in presenting the essentials in a very compact form, so that the little volume should serve as an excellent introduction to its subject. In the chapter entitled "General Considerations," especially, he has also attempted a certain measure of critical discussion that is decidedly refreshing to one who has struggled through the corresponding part of Fränkel's classic "Arzneimittelsynthese" in the hope of finding guidance rather than what is often a mere catalog of irreconcilable assertions. It is only to be regretted that the apparent unfamiliarity of the translators with the terminology of organic chemistry has permitted an absurdity such as "stearic structure of complex molecules" and so little-used a word as "acetylation" to figure in the text.

MICHAEL HEIDELBERGER.

Physiological Chemistry. Text-Book and Manual for Students. By ALBERT P. MATHEWS, PH.D., Professor of Physiological Chemistry, University of Chicago. One volume of 1042 pages, octavo, illustrated by cuts, tables and diagrams. New York: William Wood & Company. Muslin, \$4.25, net.

This is the most important new text-book and manual, written in the English language, that has been contributed to the literature of physiological chemistry in several years. It differs from its nearest competitor—if that is an appropriate expression to apply in the field of learning—both in the viewpoint and mode of presenting the subject matter. Mathews' volume is not of the cyclopedia type, like a work of ready reference to which one turns to ascertain specific facts or formulate analytical procedures. It is rather a book which, in a most delightful manner, weaves the history of the chemical aspects of physiology into the story of its modern discoveries. There is no dearth of facts, of statistics, of reactions, of formulas and descriptive biochemistry; but for the most part these are made to fit in unique ways into a dynamic conception of physiological chemistry. The functional aspects are nowhere overlooked;

and a profusion of problems of the science are pointed out by direct emphasis or by intimations which one is not likely to fail to appreciate. There is, furthermore, a novelty of statement, a freshness of presentation, quite unlike the conventional text-book that is merely compiled from current writings. The reviewer cannot refrain from citing an illustrative passage or two as an instance of these human touches. Thus:

"It is certainly not without significance that living matter is so watery and contains the salts of the sea. It would appear probable from this that living matter originated either in the sea itself or, perhaps, in some pool of water which contained, possibly in dilute form, the common salts. It has been suggested that it was in some slowly drying volcanic pool where concentration could take place, and where cyanides and other similar reactive organic compounds might have been formed by the vigorous electrical discharges accompanying the eruptions, that living matter first appeared. We would thus have sprung from the thunderbolts of Jove, if this theory is true; but we are, at any rate, the children of the sun and the sea, of Apollo and Aphrodite." (P. 15.)

Or, again, in the description of the nature of the substances concerned in intermediary metabolism:

"One way of finding out what these substances are is by combining them with something so as to make them stable and thus cause them to escape, or to pass unscathed through the fire of metabolism, coming like Shadrach, Meshach and Abednego to testify to the truth or falsity of our faith. Baumann discovered that cysteine was such an intermediary metabolic product." (P. 815.)

One could readily select a series of entertaining passages, such as those telling the story of Pasteur's discovery of the two forms of tartaric acid crystals (pp. 20-21), or the epoch-making contributions of Lavoisier, or the reasoning which led Claude Bernard to some of his discoveries—in further illustration of the exceptionally fascinating style of the book. In the detail with which some of the historical aspects of physiology are reviewed one is reminded of the earlier text-book by Gamgee.

As might be expected from a knowledge of the author's own investigations, the physico-chemical aspects of the subject are prominently treated. Speculation is not excluded so that, for example, in a fanciful discussion on the resemblance of the body to a magnet we are told (p. 268) that "All is in flux in nature. Stability is but an appearance. Our brief lives are like the fraction dt in a differential equation, infinitely brief in the time of the universe. Things appear constant when observed for such an infinitely brief time."

The question of the relative importance to be assigned to individual topics is naturally answered in accord with personal preferences. It can be said fairly that Mathews has not neglected incompletely explored topics,

of which the coagulation of the blood and the chemistry of nervous substance may serve as examples always difficult to present satisfactorily. Mathews' mode of approach is usually biological, as may be seen in discussions such as that on the formation of pepsin (pp. 353-354). Physiology and histology are woven into the chemical considerations. The presentation of disputed topics is in general commendable and well balanced. Each important chapter ends with a résumé that is useful for didactic purposes. The statements cover even very recent literature in this field. Where so much must be said in praise it can do no harm to add that the discussions concern almost exclusively the themes of animal physiology, with little regard to equally interesting features in plant biochemistry.

To the text-book proper is added a series of about 250 practical exercises including directions for the execution of approved routine methods of biochemical research. The selected experiments furnish considerable latitude to the teacher and the carefully worded directions for quantitative work offer useful assistance to the advanced worker in the physiological chemistry laboratory. It matters little whether the arrangement of this part of the book is entirely acceptable as a scheme of instruction; for in biochemistry, as in the older discipline of elementary chemistry, the competent instructor is still likely to be guided by his own ideas of sequence and proportion in the practical work. Individuality in teaching is rarely a misfortune; and the series of directions in Mathews' book segregated from the text itself make possible a maximum latitude in its use with students. The author may be assured that his welcome contribution will accomplish what he terms the main objects of every teacher: to arouse interest in the subject and to stimulate curiosity and inquiry; for he has written a readable text-book in a broadminded spirit.

LAFAYETTE B. MENDEL.

Temperatur und Lebensvorgänge. By ARISTIDES KANITZ. Berlin: Gebrüder Borntraeger. 1915. P. 175.

"The velocity of the majority of chemical reactions, at customary temperatures, is approximately doubled or trebled by a rise in temperature of ten degrees," while the majority of physical changes are affected in a much less degree at corresponding temperatures by a similar change in temperature. This fact led E. Cohen, in 1896, to throw out the exceedingly fruitful suggestion that a study of the influence of temperature changes upon the velocity of life processes might indicate whether these processes are or are not primarily the expression of underlying chemical changes.

Following the pioneer work of Herzog, Abegg, Kanitz, Loeb and Snyder, a very considerable number of investigators have in recent years entered this field of research. Among them none is more closely identi-

fied with these investigations than the author of this very timely and exhaustive monograph.

The author has brought together in form convenient for reference a truly impressive array of facts upon the foundation of which we are unquestionably entitled to base the conclusion that the vast majority of the measurable activities of living tissues are determined, in so far as the rate at which they occur is concerned, by underlying chemical processes, a conclusion which is also supported in numberless special instances by the modern developments of analytical biochemistry.

Not only are we enabled by the use of this method to establish the probable chemical nature of the processes which determine the velocity of life-phenomena, there also appears to be some ground for hoping that in the future we may be able to sharply distinguish between the chemical processes underlying different life-phenomena by means of the marked differences which subsist between the magnitudes of the effects of temperature upon them. As an example we may cite the fact that whereas the temperature coefficient of growth and development is of the customary magnitude, namely between 2 and 3, that of cytolysis and death lies between 200 and 4000 (pp. 107-110), the lower figures obtained by Goodspeed (p. 111) being probably attributable to the high temperatures employed and the complication introduced by the coagulation of proteins. This fact is in sharp disagreement with the view which has been expressed in some quarters that the death of the cell is part of the same process as, and a necessary outcome of, its growth.

The review of the literature of the subject is very exhaustive and the various articles to which reference is made are not cited, as is often the case in such monographs, as if they were all of equal value. Due deduction is made for faulty technique or inference; while exceptionally careful work is brought into the prominence to which it is entitled.

T. BRAILSFORD ROBERTSON.

Laboratory Exercises Arranged to Accompany "First Course in Chemistry." By MCPHERSON AND HENDERSON. Pp. ix + 128. Ginn and Co., 1915. Cloth, 40 cents. Biflex binder, 60 cents.

One hundred and one laboratory exercises in elementary chemistry are given. They cover the ground generally given in a good high school course in chemistry, meeting the demands of those who desire a practical application of the principles of chemistry as well as the demands of those who take chemistry as a college entrance requirement. The work in organic chemistry is naturally superficial and not thorough. The criticisms applied to the diagrams of the apparatus in the Laboratory Manual can be applied to the diagrams in the Exercises. The Exercises contain information in an appendix with regard to apparatus and materials of special value to inexperienced teachers. LILLIAN COHEN.

THE JOURNAL
OF THE
American Chemical Society

with which has been incorporated the

American Chemical Journal
(Founded by Ira Remsen)

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE PERIODIC SYSTEM AND THE PROPERTIES OF THE
ELEMENTS.

(FIFTH PAPER ON ATOMIC STRUCTURE.)

By WILLIAM D. HARKINS AND R. E. HALL.

(Copyright, 1916, by William D. Harkins.)

Received December 20, 1915.

The periodic system is the most important generalization of the facts embodied in the science of chemistry, and one of the most glaring errors in chemical pedagogy during the past fifteen years has been the neglect of this system, both in the so-called modern text-books and in the courses of instruction given in some of our universities. This has probably been due, in a large measure, to the unfortunate attempt which has been made by certain chemists to present chemistry without the use of the atomic theory. Recent remarkable discoveries made by physicists have, however, made it evident that the atomic theory and the periodic system are of supreme importance in both chemistry and physics.

The total number of elements in our present ordinary system from helium to uranium, inclusive, is 91, and with hydrogen this makes 92 elements in all. The system from helium to uranium seems to be completely known, though not all of the elements have been discovered, but nothing is known as to whether there are any elements which belong to the ordinary system and fall between hydrogen and helium in atomic

weight (possibly with atomic weights 2 and 3). Of the 92 elements, 87 have already been discovered and 5 are still unknown. Of these 5, three belong to the seventh group, two being in group VIIB, and these may be given the provisional names eka-manganese I (atomic weight about 99), and eka-manganese II (divi-manganese) (atomic weight about 188). These elements, particularly the second, should have extremely high melting points. In group VIIA eka-iodine should have an atomic weight near 219, and in group IA eka-caesium, for which Baxter made a search, but without success, should have an atomic weight of about 225. An unknown element of the rare earth group may be called eka-neodymium (atomic weight about 146).

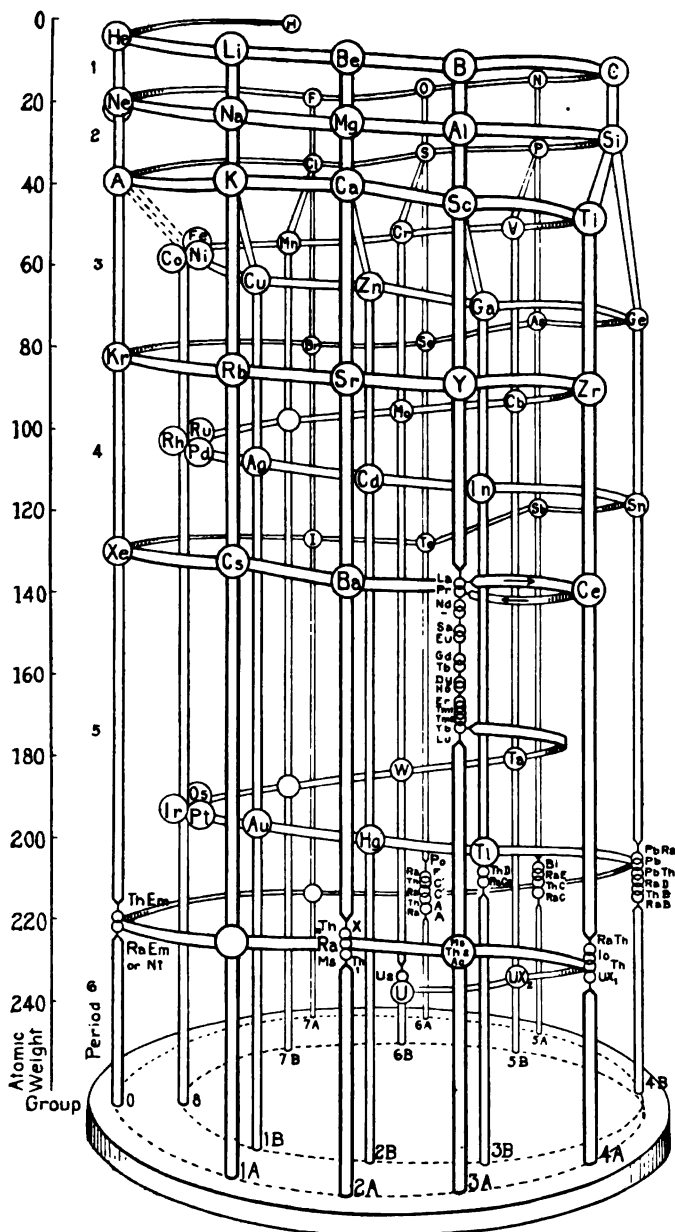
In addition to these 92 elements of the ordinary system, Nicholson assumes that there is another system of simpler elements such as protohydrogen, nebulium, protofluorine (coronium), arconium, and other elements, of atomic weights 0.082, 1.31, 2.1, and 2.9. Of these elements the spectra attributed to nebulium and arconium are found in the nebula and that of the hypothetical protofluorine is found in the corona of the sun. The evidence in favor of this simpler system is not very conclusive, but the existence of these spectra makes it evident either that some otherwise unknown elements exist in the nebulae and the corona of the sun or that the spectra are due to enhanced lines from some of the ordinary elements.¹ If such elements actually exist, they may belong to the ordinary system, or they may belong to another system, possibly with a simpler structure as Nicholson assumes. Nicholson's atomic weights were obtained from the width of the spectral lines, and also from the differences between the calculated and the observed values of the wave lengths. Both of these methods are very uncertain under the conditions of observation, so there is no conclusive evidence for the particular atomic weights which Nicholson gives.²

It has been found that the number of the element in the periodic table, beginning with hydrogen as 1, helium as 2, lithium as 3, etc.; or what is called the ATOMIC NUMBER is more characteristic of an element than its atomic weight. For example lead, with an atomic number of 82, consists of

	Atomic weight.
1. Lead from radium	206.1
2. Ordinary lead	207.20
3. Lead from thorium	208.1

¹ Merton, *Proc. Roy. Soc.*, (A) 91, 498 (1915), has obtained enhanced lines by a discharge between carbon poles in a vacuum tube, previously filled with hydrogen, which have practically the same wave length, and the same nebulous character as eight of the lines obtained in the spectrum of the Wolf-Rayet stars.

² For a more complete description and discussion of Nicholson's work see a paper on "Recent Work on the Structure of the Atom," Harkins and Wilson, *THIS JOURNAL*, 37, 1396-1421 (1915).



Periodic Table by W.D. Harkins

Note, Fig. 1.—The connections between the main and the sub-groups are shown better in Fig. 2 than in Fig. 1, since in Fig. 1 the connections were modified slightly by the artist to bring out the perspective.

	Atomic weight.
4. Radium D.....	210.1
5. Thorium B.....	214.1
6. Radium B.....	212.1
7. Lead from actinium.....	Unknown
8. Lead from actinium B.....	Unknown
9. Product of branch chain, radium series.....	210.1
10. Product of branch chain, actinium series.....	Unknown

Thus the same element may have very widely different atomic weights, but the atomic number, which presumably gives the number of positive charges on the nucleus of the atom, remains constant, and in the case of lead is 82.

A Periodic Table which Gives all of the Elements Plotted According to Their Atomic Weights, and Shows the Correct Relations from the Chemical Standpoint.

The periodic system of Mendeléeff classified the elements as well as was possible at the time when it was devised, and practically none of the more recent tables have made any improvement upon the original form, but the discoveries of the last few years make it possible to design a table which expresses the relations existing between the elements much more perfectly.

A modern table should meet the following requirements:

(1) It should plot the atomic weights so that the isotopes of such an element as lead may be included in it, their atomic weights shown, and so that the alpha and beta decompositions of the radioactive elements may be clearly depicted.

(2) It should give no blanks except those corresponding to atomic numbers of elements which remain to be discovered. The Mendeléeff table contains many blanks which can never be filled.

(3) It should in a natural way relate the main group elements to the elements in the corresponding sub-group. The principal defect of many of the periodic tables is that they have been constructed without any consideration of this important condition. A table which shows no relations between such a main group as the Be, Mg, Ca, Sr, Ba and Ra main group, and the corresponding sub-group, Zn, Cd, Hg, is not at all correct from the chemical standpoint. On the other hand, the form of the table itself should distinguish between the main and the sub-group elements. One of the disadvantages of the Mendeléeff table is that the table by its form makes no such distinction, since it throws the main and sub-groups together. However, the Mendeléeff form is much to be preferred to those given by Staigmüller, Werner and others, in which these chemical relations are not shown at all.

(4) Both the zero and the eighth groups should fit naturally into the system.

(5) All of the above relations should be shown by a continuous curve which should connect the elements in the order of their *atomic numbers*. In the ordinary form of table there is nothing to indicate the relation of one series to the next.

(6) As has been shown by Harkins and Wilson, the atomic weights are a linear function of the atomic numbers, and can be represented by the equation

$$W = 2(n + n') + 1/2 + 1/2(-1)^{n'-1},$$

where n is the atomic number and n' is ZERO for the LIGHTER ELEMENTS. It is therefore better to plot the atomic weights themselves than to plot the logarithms as has been done.¹

A modern table which meets these requirements and also shows other relationships not expressed by the ordinary form of table, may be constructed as a helix in space, or as a spiral on a plane. The space form is more nearly like the ordinary table, and is therefore to be preferred. A model of this space form, a photograph of which is shown in Fig. 3, has been constructed, and is in use in the work in inorganic chemistry in the University of Chicago. The atomic weights are plotted from the top down, one unit of atomic weight being represented by one centimeter, so the model is about two and one-half meters high.

Although the model gives the relations with extreme clearness, it is difficult to photograph it so that all of the details are visible. However, this is remedied in Fig. 1, which gives a drawing of the system. In order that the atomic weights may be plotted directly, the drawing has been made as a *vertical projection* of the model, but drawn with line perspective, and the base is given in perspective so that the table may be easily visualized in space.

The balls representing the elements are supposed to be strung on vertical rods. All of the elements on one vertical rod belong to one group,² have on the whole the same maximum valence, and are represented by the same *color*. The group numbers are given at the bottom of the rods. On the outer cylinder in Fig. 2, the electro-negative elements are represented by black circles at the back of the cylinder, and electro-positive elements by white circles on the front of the cylinder. The transition elements

¹ Stoney, *Chem. News*, 57, 163 (1888); and *Proc. Roy. Soc.*, 46, 115 (1888).

² In Figs. 1 and 2 some of the elements are represented by small, and others by larger circles. The small circles are not meant to show any difference in the elements which they represent, but are used whenever there is not room on the diagram for the larger circles. At the bottom of the table many isotopes are represented, and each intersection of the helix with a vertical group rod represents only one element, even where there are six circles as there are for the isotopes of lead. While the six circles for lead represent only one atomic number, each of the small circles on the rare earth loop represents an atomic number of its own. The three-eighth group triads, and the rare earth group resemble each other in that in these four cases the atomic number increases while the group number remains constant.

of the zero and fourth groups are represented by circles which are half black and half white. The inner loop elements are intermediate in their properties. Elements on the back of the inner loop are shown as heavily shaded circles, while those on the front are shaded only slightly.

In order to understand the table it may be well to take an imaginary journey down the helix in Fig. 2, beginning at the top. Hydrogen (atomic number and atomic weight = 1) stands by itself, and is followed by the first inert, zero group, and zero valent element helium. Here there comes the extremely sharp break in chemical properties with the change to the strongly positive, univalent element lithium, followed by the somewhat less positive bivalent element, beryllium, and the third group element boron, with a positive valence of three, and a weaker negative valence. At the extreme right of the outer cylinder is carbon, the fourth group transition element, with a positive valence of four, and an equal negative valence, both of approximately equal strength. The first element on the back of the cylinder is more negative than positive, and has a positive valence of five, and a negative valence of three. The negative properties increase until fluorine is reached and then there is a sharp break of properties, with the change from the strongly negative, univalent element fluorine, through the zero valent transition element neon, to the strongly positive sodium. Thus in order around the outer loop the second series elements are as follows:

Group number.....	0	1	2	3	4	5	6	7
Maximum valence.....	0	1	2	3	4	5	6	7
Element.....	He	Li	Be	B	C	N	O	F
Atomic number.....	2	3	4	5	6	7	8	9

After these comes neon, which is like helium, sodium which is like lithium, etc., to chlorine, the eighth element of the second period. For the third period the journey is continued, still on the outer loop, with argon, potassium, calcium, scandium, and then begins, with titanium, to turn for the first time into the inner loop. Vanadium, chromium, and manganese, which come next, are on the inner loop, and thus belong, not to main but to sub-groups. *This is the first appearance in the system of sub-group elements.* Just beyond manganese a catastrophe of some sort seems to take place, for here three elements of one kind, and therefore belonging to one group, are deposited. The eighth group in this table takes the place on the inner loop which the rare gases of the atmosphere fill on the outer loop. The eighth group is thus a sub-group of the zero group.

After the eighth group elements, which have here appeared for the first time, come copper, zinc, and gallium; and with germanium, a fourth group element, the helix returns to the outer loop. It then passes through arsenic, selenium, and bromine, thus completing the first long period of

18 elements. Following this there comes a second long period, exactly similar, and also containing 18 elements.

The relations which exist may be shown by the following natural classification of the elements. They may be divided into cycles and periods as follows:

TABLE I.

Cycle 1 = 4^2 elements.1st short period..... He — F = $8 = 2 \times 2^2$ elements.2nd short period..... Ne — Cl = $8 = 2 \times 2^2$ elements.Cycle 2 = 6^2 elements.1st long period..... A — Br = $18 = 2 \times 3^2$ elements.2nd long period..... Kr — I = $18 = 2 \times 3^2$ elements.Cycle 3 = 8^2 elements.1st very long period... Xe — Eka - I = $32 = 2 \times 4^2$ elements.

2nd very long period... Nt — U

The last very long period, and therefore the last cycle, is incomplete. It will be seen, however, that these remarkable relations are perfect in their regularity. These are the relations, too, which exist in the completed system,¹ and are not like many false numerical systems which have been proposed in the past where the supposed relations were due to the counting of blanks which do not correspond to atomic numbers. This peculiar relationship is undoubtedly connected with the variations in structure of these complex elements, but their meaning will not be apparent until we know more in regard to atomic structure.

The first cycle of two short periods is made up wholly of outer loop or main group elements. Each of the long periods of the second cycle is made up of main and of sub-group elements, and each period contains one-eighth group. The only complete very long period is made up of main and of sub-group elements, contains one-eighth group, and would be of the same length (18 elements) as the long periods if it were not lengthened to 32 elements by the inclusion of the rare earths.

The first long period is introduced into the system by the insertion of iron, cobalt, and nickel, in its center, and these are three elements whose atomic numbers increase by steps of one while their valence remains constant. The first very long period is formed in a similar way by the insertion of the rare earths, another set of elements whose atomic numbers increase by one while the valence remains constant.

In this periodic table the MAXIMUM valence for a group of elements may be found by beginning with ZERO for the zero group and counting

¹ If elements of atomic weights two and three are ever discovered then the zero cycle would contain 2^2 elements, and period number one should then be said to begin with lithium. Such extrapolation, however, is an uncertain basis for the prediction of such elements.

toward the front for POSITIVE valence, and toward the back for NEGATIVE valence.

The negative valence runs along the spirals toward the back as follows:

0	-1	-2	-3	-4
Ne	F	O	N	C
A	Cl	S	P	Si

Beginning with helium the relations of the maximum theoretical valences run as follows:

Case 1. He — F..... 0, 1, 2, 3, 4, 5, 6, 7, but does not rise to 8. Drops by 7 to 0.

Ne — Cl.... 0, 1, 2, 3, 4, 5, 6, 7, but does not rise to 8. Drops by 7 to 0.

Case 2. A — Mn.... 0, 1, 2, 3, 4, 5, 6, 7, 8, 8, 8. Drops by 7 to 1.

Fe, Co, Ni.

Case 1. Cu — Br

Case 2. Kr — Ru, Rh, Pd.

In the third increase, the group number and maximum valence of the group rise to 8, three elements are formed, and the drop is again by 7 to 1.

Thus in every case when the valence drops back the drop in maximum group valence is 7, either from 7 to 0, or from 8 to 1.¹ This is another illustration of the fact that the eighth group is a sub-group of the zero group. The valence of the zero group is zero. According to Abegg the contra-valence, seemingly not active in this case, is eight.

In Fig. 2 the table is divided into FIVE DIVISIONS by four straight lines across the base. These divisions contain the following groups:

Division.....	0	1	2	3	4
Groups.....	0,8	1,7	2,6	3,5	4,4

The two groups of any division are said to be complementary. It will be seen that the sum of the group numbers in any division is equal to 8, as is also the sum of the maximum valences. The algebraic sum of the characteristic valences of two complementary groups is always zero. *In any division in which the group numbers are very different, the chemical properties of the elements of the complementary main groups are very different, but when the group numbers become the same, the chemical properties become very much alike.* Thus the greatest difference in group numbers occurs in division 8, where the difference is 8, and in the two groups there is an extreme difference in chemical properties, as there is also in division 1 between Groups 1 and 7. *Whenever the two main groups of a division are very different in properties, each of the sub-groups is quite different from*

¹ It should be noted that while in the change from the seventh to the zero group the valence always drops to zero, in the change from the eighth to the IB group, there is a tendency to drop only part way, that is to a valence of 3 for gold (or silver), or to 2 for copper, though these elements also show the valence of one normal for the group, but by the time Group IIB is reached in zinc, cadmium, and mercury, the valence comes to the normal value, which is 2 for this group.

its related main group. Thus copper in Group IB is not very closely related to potassium group IA in its properties, and manganese is not very similar to chlorine, but *as the group numbers approach each other the main and sub-groups become much alike.* Thus scandium is quite similar to gallium in its properties, and titanium and germanium are very closely allied to silicon.

One important relation is that *on the outer cylinder the main groups IA, IIA, IIIA, become less positive as the group number increases, while on the inner loop the positive character increases from Group IB to IIB, and at the bottom of the table the increase from IIB to IIIB is considerable.* Thus thallium is much more positive than mercury. It has already been noted that in the case of the rare earths also the usual rule is inverted, that is the basic properties decrease as the atomic weight increases.

Another important relation between the members of the main and the sub-groups is that when the atomic volume of the elements in the main group is large, the atomic volume of the elements in the corresponding sub-groups is small, and as the atomic volume for the main group decreases, that for the sub-group increases. Thus, the zero group elements have very high atomic volumes, while those for the corresponding sub-groups (Group VIII) are very low. The same is true of the potassium group (high atomic volume) and the copper group (low atomic volume). On the other hand, the members of Groups IVA and IVB do not differ materially in regard to this property. The difference in chemical properties between main and sub-groups is just that which should result from their differences in atomic volume. From this standpoint it may be considered that the difference in chemical properties between the main and the sub-group elements is the result of the fact that the long periods for the 'cohesional properties (atomic volume, etc.) are twice the length of the series which condition the valence. In cycle 1 (short periods 1 and 2), the valence and the cohesional properties have periods of exactly the same length, so both of the periods represent main groups or outer cylinder elements, but in cycle 2 the valence passes through two periods while the cohesion (Fig. 12) is passing through one, so here sub-group elements appear for the first time. While the cohesion does not fix the valence, it does affect the chemical affinity. The increase in the basic properties of the sub-group elements as the group number increases from IB to IIIB, seems to be related to the occurrence of the secondary minimum in cohesion (and melting points) which comes in group IIIB. (See Fig. 8.)

On the first inner loop the positive character of the metal, as measured by the potential between the ions of the elements in unimolar solutions and the metal itself, decreases from manganese to copper, and then increases very rapidly in the one step to zinc, as is shown below in Table IA.

TABLE IA.—POSITIVE CHARACTER OF THE METALS IN SOLUTIONS WITH THEIR
BIVALENT IONS.

Mn	= +0.798 volt
Fe	= +0.122 volt
Co	= -0.0138 volt
Ni	= -0.108 volt
Cu	= -0.606 volt
Zn	= +0.493 volt

The Rare Earths.

There are some questions concerning the placing of the rare earth elements which are of minor importance, and may be settled by each user of such a table to suit his own convenience. Thus cerium, following the usual custom, has been put in the fourth group. This makes an extra small loop in the table which could be avoided by placing cerium in the third group with the other rare earths. That after passing lanthanum there is a tendency to swing into the fourth group with cerium, and then with praseodymium and neodymium to swing back into the third group, is indicated by the fact that cerium forms an extremely stable dioxide (CeO_2); praseodymium forms a dioxide less stable than manganese dioxide, which is itself not extremely stable; while neodymium is said to form a higher oxide only when mixed with cerium and praseodymium, or perhaps not at all; and samarium forms no higher oxide.

On the other hand, the position of the rare earths as a whole is very important. Their valence, the difficulty with which they are separated from yttrium, and their chemical reactions clearly indicate that they should be related to the third group, but put on a loop of their own. In many periodic tables, for example, even in the otherwise very good table given by Rydberg,¹ thulium is put in the chlorine family, samarium in the eighth group, europium in the silver group, etc. The system presented here shows that such a procedure is altogether unjustified, for there are not enough rare earths to go around the table, since there are *four less than the required number*, even when the one unknown rare earth is counted. That the number of elements in this, the fifth period, is taken correctly as 32 can be seen from the work of Moseley upon the X-ray spectra of the elements, and is indicated also by the regularity in the numerical relations between the number of elements in the different periods as already pointed out by Table I. If the rare earths are to be distributed around the table, then there should be a considerable variation in their atomic volumes. Although the atomic volumes of very few of the rare earths have been determined, the data are available for the calculation of the molecular volumes of a number of the chlorides and oxides. Thus the molecular volumes of the chlorides are as follows:

¹ Hicks, *Phil. Mag.*, [6] 28, 139 (1914).

LaCl ₃	63.8
CeCl ₃	62.9
PrCl ₃	60.8
NdCl ₃	60.6
SmCl ₃	57.5
GdCl ₃	58.3
TbCl ₃	61.1
DyCl ₃	73.3

In order to understand the interpretation of these molecular volumes in terms of the atomic volumes of the rare earths, their basic properties must be taken into account. The order of the rare earths in terms of their basic properties is as follows, where the most basic element is given first: Lanthanum, praseodymium, neodymium, cerium^{III}, (yttrium), samarium, gadolinium, terbium, holmium, erbium, thulium, and ytterbium. Thus, exactly the opposite of the usual rule holds, for in this rare earth group the basic properties decrease just in the order in which the atomic weights increase. Cerium is the only element which falls out of the regular order, and it is the element which in the table (Fig. 2) is classified differently from the others. If the rare earth elements were to be distributed around the table, then samarium, europium, and gadolinium would fall in the eighth group, and therefore should have minimum atomic volumes. That these are the elements of the rare earths which *do have minimum atomic volumes* is indicated by the molecular volumes of the chlorides. The increase in the molecular volume of the chlorides in the case of dysprosium chloride seems to indicate that there is a *minor peak* in the atomic volumes beyond this point. It would be interesting in this connection to know the molecular volumes of ytterbium and lutecium trichlorides, or much better of course, the atomic volumes of ytterbium and lutecium. These facts may be taken to indicate that when in the formation of the elements the 57th element, lanthanum, belonging to the third group, is passed, there is a tendency for the elements to form according to the usual rule, that is, that the valence shall increase by steps of one and the atomic volume shall vary as usual. From this point on, the tendency for the atomic volumes to hold to the regular system of variation is quite likely partly effective. On the other hand, the valence succeeds only in rising by one to four in the case of cerium, the 58th element, and then only for a few of its compounds. With praseodymium and neodymium the valence returns toward three, and for samarium and the remainder of the group the highest valence seems to be constant at three. Such relationships as these need not seem peculiar, since the valence is usually supposed to be due to only a few of the electrons in the atom, in this case to three electrons, while the atomic volumes are undoubtedly conditioned by the other electrons in the atom, external to the nucleus, as well. That the atomic volumes do not wholly follow

the ordinary rule is shown by the fact that the atomic volumes of samarium, europium, and gadolinium do not fall nearly so low as the ordinary eighth group elements.

The exceptional behavior of the rare earths in regard to their basic properties may be explained in somewhat the same way as the probable atomic volume relations. Just before coming to the rare earths the basic properties decrease rapidly from caesium, to barium, and to lanthanum. This decrease persists through the rare earth loop, which may be called a tertiary loop, but probably the opposing tendency, that is for the elements of any one main group to increase in basic properties, also has an effect, for the rare earths do not decrease in basic properties with anything like the rapidity which would be apparent if they were distributed around the table in the order of the other elements.¹ If they were thus distributed, either ytterbium or lutecium should be chemically similar to iodine, and that is not the case. The elements on the outer cylinder in Table I may be said to be on primary loops, the inner loops may be designated as secondary, and the rare earths as a tertiary loop. This tertiary loop connects lanthanum and cerium to tantalum, and could be drawn inside the outer cylinder, but since the valence of the rare earths is three, it has been thought best to show them on the vertical rod which represents this valence, in order to make the figure as simple as possible. Thus, the rare earths belong in a sense to the third group, but bear a somewhat peculiar relationship to the other elements of the group.

Supposed Imperfections of the Periodic System.

A great deal of attention has been given in papers in journals, and in books, to what have been called the imperfections in the periodic system. Among the most emphasized of these has been the fact that when arranged in a periodic table in the order of their properties, a few elements, argon, cobalt, and tellurium, are not in the strict order of their atomic weights. It has now been shown by Moseley that the elements in the periodic system are not plotted according to the *order of their atomic weights*, but according to the *order of their X-ray spectra*, or what is called the *atomic number*. According to a theory developed by Rutherford, the atomic number represents the number of positive charges on the nucleus of the atom. If this is true THE PERIODIC SYSTEM SHOWS THE RELATION BETWEEN THE PROPERTIES OF THE ELEMENTS AND THE NUCLEAR CHARGE OF THE ATOMS, AND THIS IS PRESUMABLY EQUAL TO THE NUMBER OF NEGATIVE ELECTRONS EXTERNAL TO THE NUCLEUS. *It is probably the spacing and arrangement of these external electrons which determines the chemical properties*

¹ In this decrease of basic properties with increase in atomic weight inside one group the rare earths act in the same way as the elements on the front of the inner loop, and it is quite possible that it is better to state the fact thus than to give the somewhat involved explanation expressed above.

and those physical properties of the elements which are not functions of the nuclear mass. When considered in this way it is apparent that there remain no imperfections in the system to be explained, for it is not necessary that the mass of the atom shall vary just as the nuclear charge. Neither is it to be supposed that all of the properties of the atoms should vary according to the same function of this charge.

Explanation of Regularities and Irregularities in the Atomic Weight Relations.

In a recent series of papers¹ Harkins and Wilson have presented a theory in regard to the formation of complex from simple atoms, which may be used to explain some of the remarkable relations in the atomic weights, such as exist in one of the triads of Dobereiner.

	At. wt.	Difference.
Lithium.....	6.94	
Sodium.....	23.00	16.06
Potassium.....	39.10	16.10

In addition to the occurrence of the difference 16 in this triad it is found that the atomic weights of six of the eight elements of the third series may be found by adding 16 to the atomic weights of the elements just above them. Between Series 3 and 4, two of the differences are again 16, and five amount to 20. The greatest common divisor of these numbers is 4, and this is assumed to mean that in general the differences in mass between the atoms of any one group in the periodic table are due to differences in the number of helium atoms, of mass 4, which have been used up in their formation. The proof of this system can not be given here, but can be found in the papers to which reference has been made.

The explanation of these regularities is made more apparent by Table II.

The explanation for the *irregularities* in the atomic weights may be illustrated by citing the case of argon, which has an atomic weight greater than potassium, which comes just after it. This irregularity is due to the tendency for the atoms as they grow larger to take on helium units more rapidly. If argon followed the rule of aggregation as followed in Series 2, its mass would be 36, but the tendency to take on helium atoms more rapidly characterizes Series 4. The elements of the third series are formed from those of the second by the addition of four helium units, but this difference grows to five helium units between Series 3 and 4. Thus from neon to argon is 5 helium units or 20, and $20 + 20$ gives 40, the atomic weight of argon. Only in the cases of potassium and calcium does the increment between the series fall back to that between the sec-

¹ THIS JOURNAL, 37, 1367-96 (1915); *Phil. Mag.*, 30, 723-34 (1915).

TABLE II.—A PERIODIC SYSTEM REPRESENTING IN GENERAL THE SYSTEM ACCORDING TO WHICH THE ELEMENTS HAVE BEEN BUILT UP FROM HYDROGEN AND HELIUM.

H detd. = 1.0078.

Group.	0.	1.	2.	3.	4.	5.	6.	7.	8.	
Series 2.	He	Li	Be	B	C	N	O	F		
	He	He+H ₄ .	2He+H.	2He+H ₄ .	3He.	3He+2H.	4He.	4He+H ₄ .		
Calc.	=H ₄	7	9	11	12	14.	16	19		
Detd.	4	6.94	9.1	11	12	14.01	16	19		
Series 3.	Ne	Na	Mg	Al	Si	P	S	Cl		
	5He.	5He+H ₄ .	6He.	6He+H ₄ .	7He.	7He+H ₄ .	8He.	8He+H ₄ .		
Calc.	20	23	24	27	28	31	32	35		
Detd.	20	23	24.3	27.1	28.3	31.02	32.07	35.46		
Series 4.	A	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co
	10He.	9He+H ₄ .	10He.	11He.	12He.	12He+H ₄ .	13He.	13He+H ₄ .	13He.	14He+H ₄ .
Calc.	40	39	40	44	48	51	52	55	56	59
Detd.	39.88	39.1	40.07	44.1	48.1	51	52	54.93	55.84	58.97

Increment from Series 2 to Series 3 = 4 He.

Increment from Series 3 to Series 4 = 5 He. (For K and Ca = 4 He.)

Increment from Series 4 to Series 5 = 6 He.

ond and third series, that is to 4 times 4 or 16. In other words, potassium has the atomic weight which it should have according to the rule that the atomic weight increases four units for each increase of two in the atomic number. Argon has a weight four more than this, due to the taking on of one too many helium units, which, however, is what all of the fourth series elements do except potassium and calcium.

The Radioactive Elements.

The periodic table presented in this paper is admirably adapted to show the relations existing between the radioactive elements as expressed by the rule of Soddy and Fajans. These relations are expressed on the space model (Fig. 3), and better still, on a space model on which the vertical scale is made much greater, for example, four centimeters to one unit of atomic weight. Fig. 4 gives an enlarged view of the bottom part of the table shown in Fig. 3, and shows the elements from tantalum to uranium. In this figure the elements derived from thorium by disintegration are designated by rectangles, and the members of the radium series, by sections or circles. The actinium series has not been included, since the atomic weights are not known, but they can easily be added as soon as the atomic weight of actinium is determined. This series has been included in Fig. 5 but the scheme is doubtful so far as the actinium series is concerned.

Uranium (atomic weight 238.2), the parent of the members of the radium series, belongs to Group VIB on the back of the inner loop. It shoots off an alpha particle (the doubly positively charged nucleus of a helium atom) and changes into uranium X₁ (at. wt. 234.2), which belongs to Group IVA. This gives off a beta particle and changes into uranium

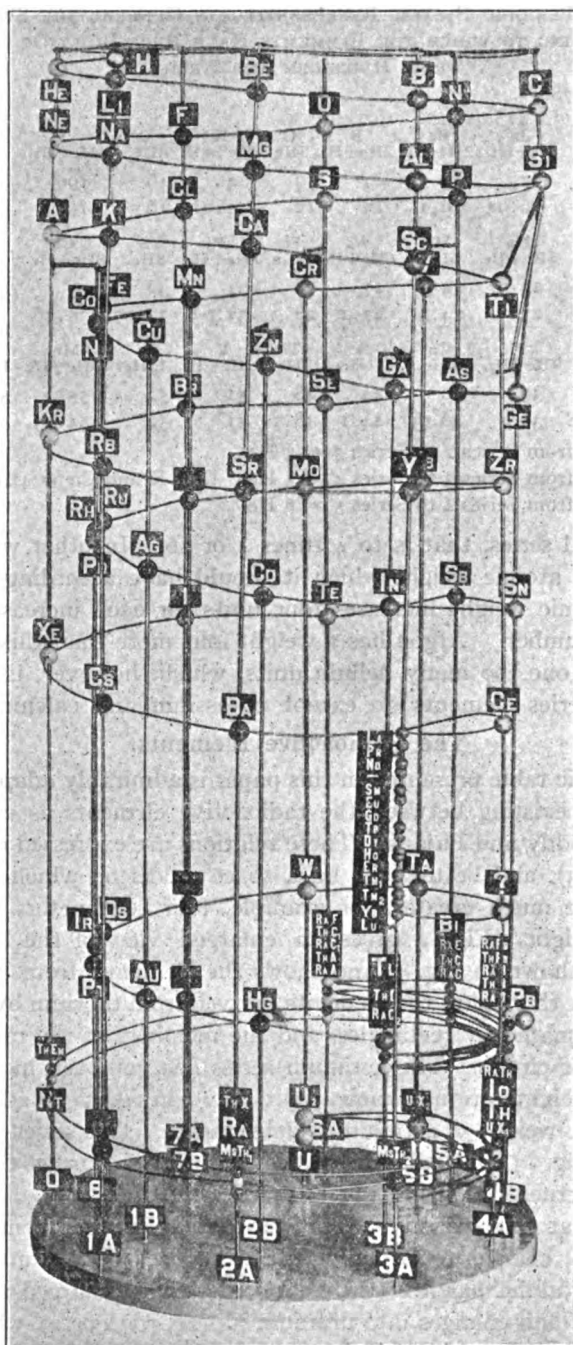


Fig. 3.

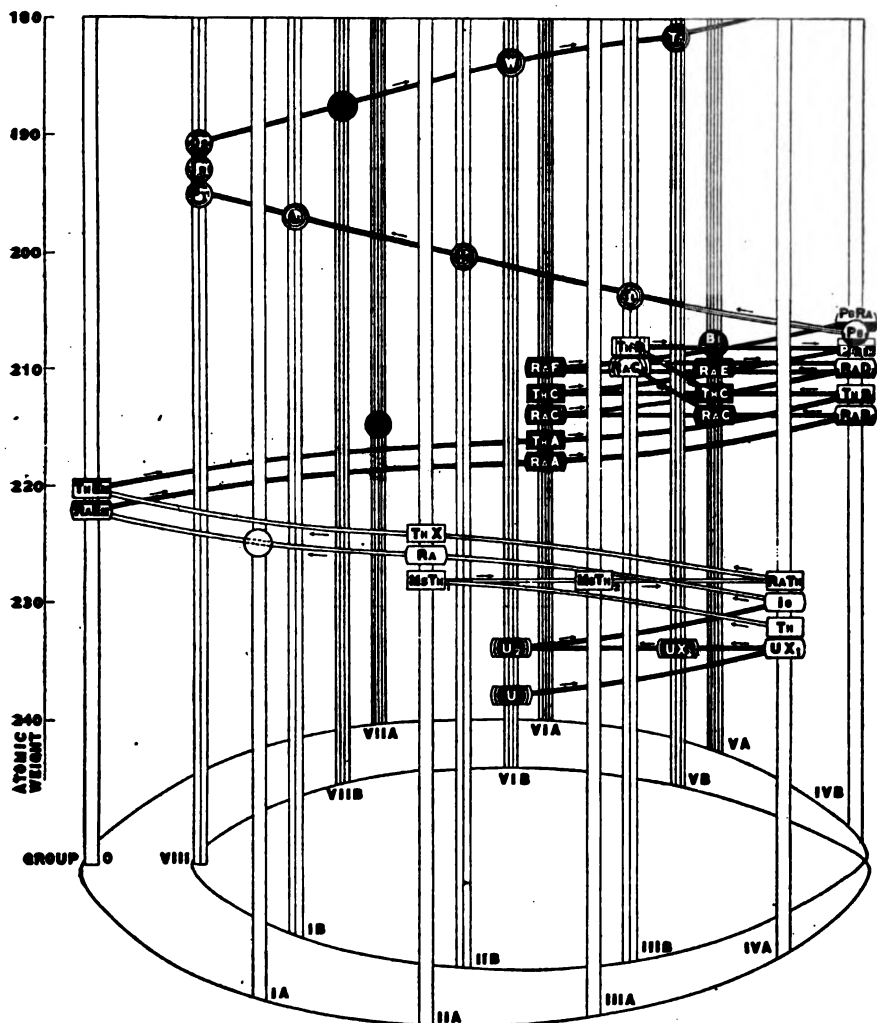


Fig. 4.—Periodic system showing the radioactive elements of the thorium and radium series.

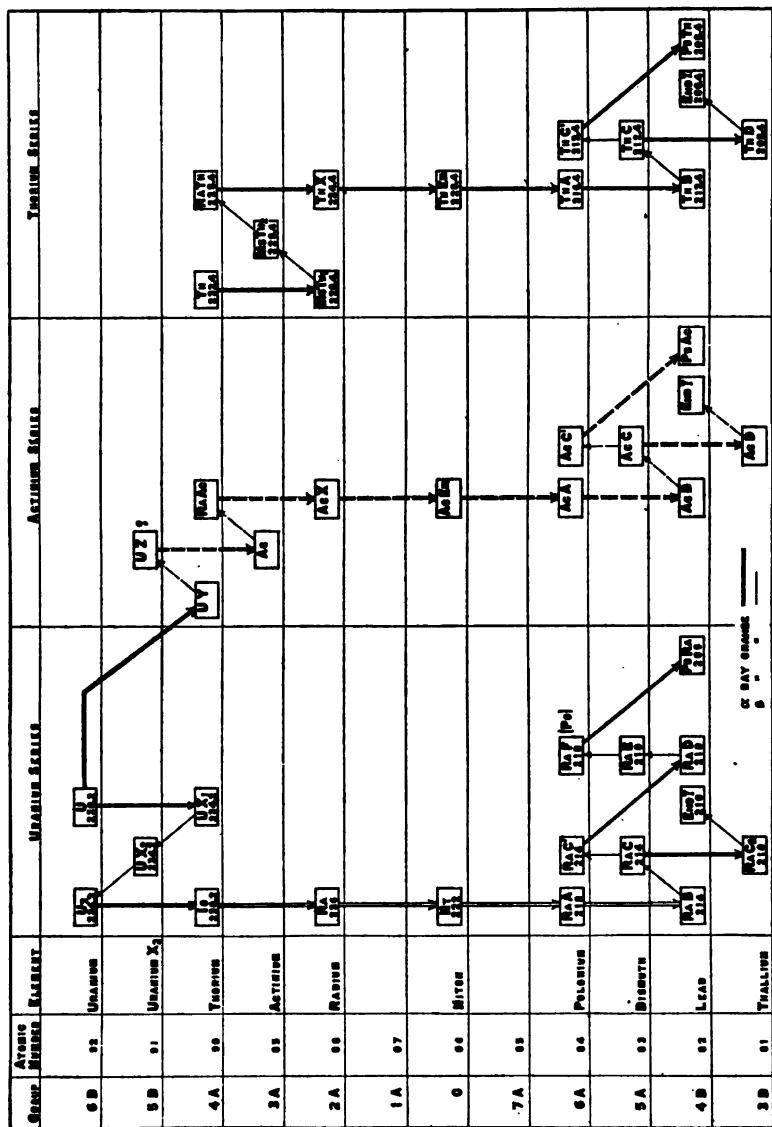


Fig. 5.—Table of the radioactive elements. Note: A new determination of the atomic weight of thorium gives 232.2, so the decimal in the thorium series should be 0.2. The actinium series is not yet fixed with any certainty.

X_2 (Group VB) without a change of atomic weight. A second beta change converts uranium X_2 into uranums, isotopic with uranium and with an atomic weight four less. This is converted into ionium by an alpha

TABLE III.—PERIODS OF THE RADIOACTIVE ELEMENTS, WITH ISOTOPES CLASSED TOGETHER.

At. No.	Isotopes of	Name of isotope.	Atomic weight.	Ray.	Period.		
92	Uranium	Uranium ₂	234.2	α	2 million years	1	
		Uranium	238.2	α	5 billion years		
91	Uranium X ₂	Uranium X ₂	234.2	β	1.15 minutes	2	
90	Thorium	Radiothorium	228.2	α	2.02 years	3	
		Ionium	230.2	α	200,000 years		
		Thorium	232.2	α	18 billion years		
		Uranium X ₁	234.2	α	24.6 days		
		Radioactinium	...	α, β	19.5 days		
		Uranium Y	1.5 days	4	
89	Actinium	Meso-thorium 2	228.2	β	6.2 hours		
		Actinium	5	
88	Radium	Thorium X	224.2	α	3.64 days		
		Radium	226.2	α	1730 years		
		Meso-thorium 1	228.2	α	5.5 years		
		Actinium X	11.4 days		
87	(Unknown)						
86	Niton	Thorium emanation	220	α	54 seconds	6	
		Radium emanation	222	α	3.85 days		
		Actinium emanation	...	α	3.9 seconds		
85	Unknown						
84	Polonium	Radium F	210	α	136 days	7	
		Thorium C'	212	α	10^{-11} seconds		
		Radium C'	214	α	10^{-8} seconds		
		Thorium A	216	α	0.14 second		
		Radium A	218	α	3 minutes		
		Actinium A	...	α	0.002 second		
81	Thallium	Thorium D	208	β	3.1 minutes	8	
		Radium C ₂	210	β	1.4 minutes		
		Actinium D	...	β	4.71 minutes		
		Bismuth	208	...	Extremely long		
83	Bismuth	Radium E	210	β	5 days	9	
		Thorium C	212	α, β	60 minutes		
		Radium C	214	α, β	19.5 minutes		
		Actinium C	...	α	2.15 minutes		
82	Lead	Lead from Ra	206	...	Extremely long	10	
		Lead from Th	208	...	Extremely long		
		Radium D	210	β	16.5 years		
		Thorium B	212	β	10.6 hours		
		Radium B	214	β	26.7 minutes		
		Actinium B	...	β	36.1 minutes		
		Lead from secondary branch of radium series					
		Lead from secondary branch of actinium series					

change, and this in turn changes into radium by another alpha transformation. These changes, and the others until the disintegration ends with lead from radium (Pb Ra), can be easily traced by following the lines in the table. In each loss of an alpha particle the atomic weight decreases by approximately four, and the valence and group number both decrease by two. Each loss of a beta particle increases the valence and group number by one, but causes no change of atomic weight.

The half-period of a radioactive element is the time in which one-half of the element would disintegrate. The half-periods of each set of isotopes are given in Table III.

The table giving the periods of the radioactive elements shows that the period for any one isotope varies with the atomic weight in some regular way. It is difficult to make any comparison in this sense which includes the members of the actinium series, since their atomic weights are unknown. In the case of the isotopes of thorium, thorium itself has the longest period, and thus decreases in each direction as the atomic weight decreases or increases. The periods of the isotopes of lead decrease as the atomic weight increases, and the same is true of the periods of bismuth and its isotopes. However, in the case of the isotopes of polonium (Radium F), Thorium C' has the minimum period, and the period increases on each side as the atomic weight either increases or decreases.

The Nature of Isotopes.

It is now known,¹ as has already been pointed out, that a single element, with a single atomic number, may consist of several different kinds of atoms, which are alike in that they seem to have the same nuclear charge, and therefore presumably, the same number of external negative electrons. Isotopes seem to be identical chemically, and so far as is known they give identically the same spectrum, but they may or may not differ in certain physical properties, such as the melting points. Thus neon and meta-neon, which differ in atomic weight by two, were separated by diffusion. On the other hand, Soddy finds that lead from thorium and ordinary lead have the same atomic volume, that is, the lead obtained from thorium minerals is denser than ordinary lead in the ratio of the atomic weights. Richards² has found that the lead from radium is also different in density from ordinary lead. Such isotopes as these differ in those properties which are functions of the mass of the particle, and they may be called isotopes of the first class. A second kind of isotopism is that in which there is no difference in mass except that due to a difference in the packing effect. Thus Radium D and the end number of the secondary radium disintegration series, which is as yet unnamed, have the same atomic weight except for the very slight difference

¹ *Le Radium*, 10, 171.

² *THIS JOURNAL*, 38, 221 (1916).

in mass due to a difference in the internal energy of the atoms, and this difference is so slight as to be experimentally undetectable, so these may be called isotopes of equal mass. Also, though the atomic weight of actinium has not been determined as yet, enough is known of its disintegration series so that it is practically certain that a number of actinium derivatives show this form of isotopism with members of the radium series. Thus if we assume that the atomic weight of actinium is 230, then radio-actinium and ionium which are isotopic must both have atomic weights of 230, but the latter has a half-period of 200,000 years, and the former of only 19.5 days, so there is a very great difference in stability. Even if the atomic weight of actinium is different, it will be seen from Fig. 5 that some of the other members of the two series must show this form of isotopism.

Isotopes of approximately equal atomic mass are derived from the same ancestral atom, that is from either uranium or thorium, for no thorium disintegration product is known which has the same mass as a uranium disintegration product. In the formation of isotopes of this class, different amounts of energy seem to be given out, so they must differ in internal energy, and to a greater or lesser extent in stability. It does not seem improbable that this difference may be due to the expulsion in the different cases of alpha and beta particles which lie in structurally different positions in the nucleus.

The Nuclei of Complex Atoms.

According to the above views, and those advanced by Harkins and Wilson in the first four papers of this series, which advanced the theory that the nuclei of complex atoms are built up from hydrogen and helium nuclei according to the system presented in Table II, it may be assumed that the chemical nature of the atom is independent of the number of particles present in the nucleus of the atom, and therefore of the mass of the atom, and is also independent of the structure of the nucleus, so long as the structure does not affect the nuclear charge. The chemical properties of the atom are, according to this view, dependent wholly upon the nuclear charge. When the complex nucleus is built up from only a few hydrogen and helium nuclei, there are not many stable arrangements which give a single nuclear charge, but when the nuclei are very complex, the possible number of more or less stable structures should be considerably increased. Therefore it is to be expected, as was found by Harkins and Wilson, that the atomic weights of the lighter elements should follow some regular system with only small deviations, but that these deviations should become much more considerable in the case of the more complex heavier elements. In other words, isotopes should be found much more abundantly among the heavy than among the light elements. The fact that the isotopes of any two different series differ

in atomic weight by about two units, suggests that the difference is caused by the presence of two hydrogen atoms in one set of atoms, and their absence from the other. As examples it may be remembered that neon and meta-neon are supposed to differ in atomic weight by two units, and within the accuracy to which the atomic weight of thorium has been determined, there is the same difference between two adjacent isotopes of the thorium and the uranium series.

A Plane or Spiral Form of the Periodic Table.

The periodic table presented in this paper is a space form, though it is easily represented on a plane as in Fig. 2. The space form may, however, be easily converted into a plane diagram by plotting the atomic weights radially from a point in a plane. This gives the table represented in Fig. 6. While this spiral form of table does not seem to the writers to be so well adapted to general use as the space form, it does show exactly the same relations between all of the chemical and physical properties of the elements.¹ This table is different, too, from other spiral tables, for none of the earlier tables have been so constructed as to classify the elements correctly. Thus, for example, the spiral table given in Erdmann's chemistry classifies Ne, Ni, Rh, and Ir, in one group, Na, Cu, Ag, Gd, and Au in another, and Li, K, Rb, Cs, leaving out Na, in a third. These are obviously improper classifications. The error in all previous spiral tables has been due to a failure in plotting to distinguish between the long and the short periods. In Fig. 7 the short-period elements occur only above the median line, while the long periods make a continuous line both above and below.

It is interesting to note that around the long periods the group numbers run 0, 1A, 2A, 3A, 4A, 5B, 6B, 7B, 8, 1B, 2B, 3B, 4B, 5A, 6A, 7A, 0, which is exactly the order in the tables presented in Figs. 2 and 4. Table 7 is the first spiral table to give the chemical relations correctly.

The Relation between the New Form of the Periodic Table and the other Modifications.

In his book entitled "New Ideas on Inorganic Chemistry," Werner,² in discussing the periodic system, says:

"... up to the present the satisfactory grouping of the iron group and the rare earths appears to be almost impossible. Most of these difficulties are not difficulties of principle, *i. e.*, they are not to be referred to the nature of the metal in question, but rather to the particular arrangement adopted to illustrate the periodic occurrence of chemically allied elements.

"The principle chosen by Mendeléeff, of bringing analogous elements as near as possible together in order to bring out the less evident similarities which exist between such elements, has been followed by his successors. This process has led to a crowding

¹ Except that it does not show so well the relations between what have been called complementary groups.

² English edition, Longmans, 1911, p. 4.

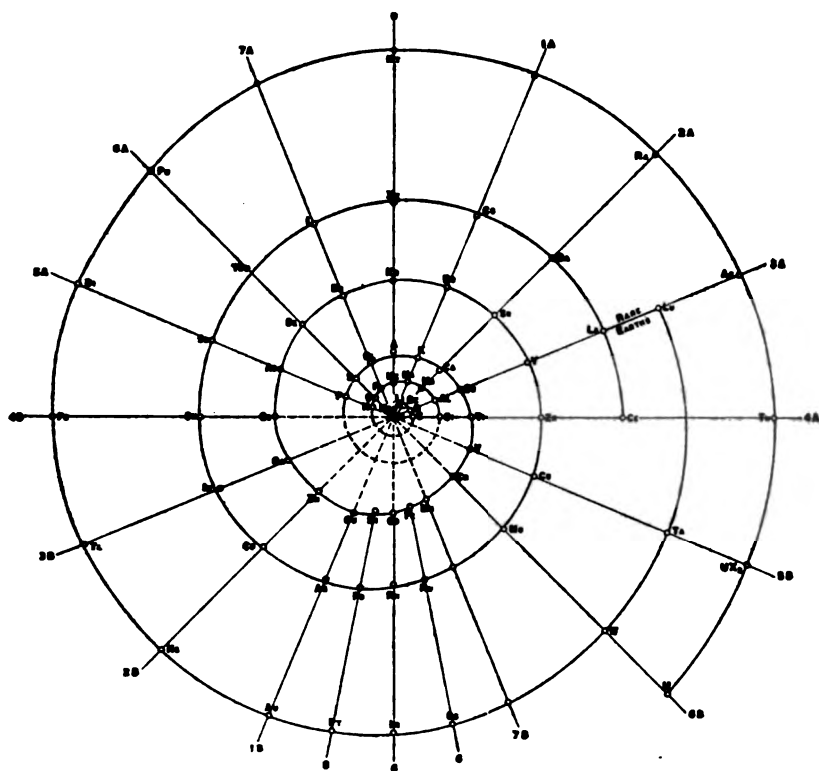


Fig. 6.—A spiral form of the periodic table.

together (*Ineinanderschachtelung*) of the elements which is harmful to the synoptical character of the periodic system, and this is especially true when we consider only the less important analogies: the result of equal valencies. This compression of the elements into the least possible space is the chief cause of many elements not finding a suitable position in Mendeléeff's scheme. This remark is particularly applicable to the eighth group, and to the metals of the rare earths."

However, in finding a remedy for the defects which he discusses, Werner goes to the opposite extreme, and places the elements in such a way that many important analogies become obscured. By placing the elements farther apart on the helix, but close together in space, the new table is able to combine all of the advantages, and to eliminate the disadvantages of such widely different forms. The relation between these different tables is discussed below.

If, in Figs. 1, 2, or 3, the lines of the helix are cut between the seventh and the zero groups, and between the eighth and the 1B groups, the table when spread out on a plane becomes much like that of Mendeléeff, except that there are no blanks except those which correspond to atomic numbers, that the rare earths are arranged differently, and that the drawing would still show the distinction between the main and the sub-groups. However, if all of the connecting lines are taken out, the table becomes essentially that of Mendeléeff. If the helix is cut only between the seventh and the zero groups, unrolled, and laid on a plane, it takes on the general form of the Carnelley-Richards table,¹ which is probably the best of all of the plane tables except that of Mendeléeff. If the helix is cut between carbon and nitrogen, between silicon and phosphorus, and between the seventh and the zero groups, and again spread on a plane, it gives the form attributed to Meyer, to Palmer, and to Staigmüller.² The essential advantage claimed by Staigmüller is that in his table a line separating the non-metals and the metals may be easily drawn, and that the non-metals fall into one group in the table. The elements which he classifies as non-metals are B, C and Si, N, P (and partially As); O, S, Se (and partly Te); F, Cl, Br, and I; and also He, Ne, A, Kr, and Xe. If this is an advantage of the Staigmüller table, it is much more an advantage of the new space form here presented, as in our table the non-metals are much more closely grouped, as they lie entirely in one group on the outer cylinder, and all except B, C and Si, lie at the back.

Werner's table,³ except for the arrangement of the rare earths, may be obtained by cutting the helix so that the elements in each of the following pairs of elements become separated: Li and Be, Na and Mg, Ca and Sc, Sr and Y. It should also be cut between the 0 and 1A groups, and then spread out on a plane. The transformation into the form devised by

¹ *Chem. News*, 78, 193-5 (1898).

² Nernst's "Theoretische Chemie," *Siebente Auflage*, p. 184.

³ *Ibid.*, p. 185.

Walker¹ is also a simple one, since the spiral needs only to be cut between the seventh and zero groups, and the vertical rods severed between K and Rb, between Ca and Sr, Sc and Y, Si and Ti, P and V, S and Cr, and between Cl and Mn.

As has already been seen, the new table may be represented on a plane as a spiral, or in space as a figure 8. The use of a figure 8 space form of table was first suggested by Crookes,² but the arrangement of the elements in his table was very different. The use of a figure 8 diagram has been advocated by Soddy,³ who gives the best table previously devised but such a representation obscures both what have been called the complementary relations and the relations between the main and the sub-groups.

While in the development of the periodic table in space as presented in this paper, no use was made of any previously devised system except that of Mendeléeff, it will be seen that it is a generalized form, of which the Mendeléeff, Carnelley-Richards, Werner, Staigmüller, and other modifications, are special cases, each of which expresses certain relations well, but others poorly or not at all. The space form eliminates the disadvantages of the different plane tables, and at the same time combines their advantages. That at first sight it seems more complex than the Mendeléeff table is due to the fact that it classifies all of the elements, but it is actually more simple, since it contains no blanks except the five which correspond to atomic numbers. Experience has shown that students who have no previous knowledge of the Mendeléeff table find the space form the more simple, at least when they have the model to use in their study.

COHESIONAL PROPERTIES.

Atomic Volumes, Melting Points, and Related Properties.

In Fig. 1 the elements of highest atomic volume lie at the left of the outer loop, while the elements of lowest atomic volume lie at its right (carbon, silicon and aluminium) as long as the outer loop persists at the extreme right, and when the outer loop disappears at this extremity, the line of lowest atomic volume jumps over to the left end of the inner loop. To show these atomic volume relations somewhat more simply the table has been drawn in the form given in Fig. 7. From the standpoint of the chemical relations this latter table is much less perfect than the former, but it has the one advantage that the elements of high atomic volume are at the left of the table, and those of low atomic volume are at the right, so if this table is hung with its left side as the top, the loops take the general form of

¹ *Chem. News*, 63, 251-3 (1891).

² *Ibid.*, 78, 25 (1898); *Proc. Roy. Soc.*, 63, 408-11 (1898); and *Z. anorg. Chem.*, 18, 72-6 (1898).

³ *Chemistry of the Radioactive Elements*, Part II, p. 11.

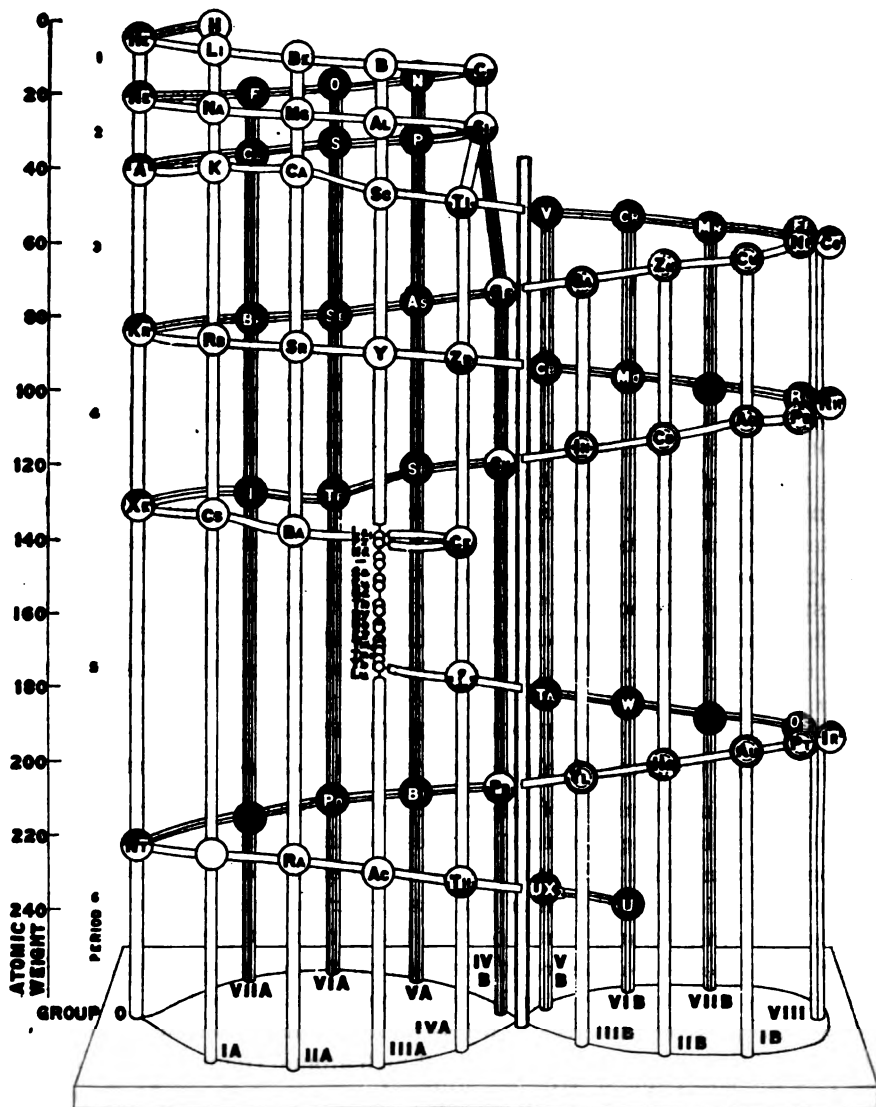


Fig. 7.—Periodic table modified so as to show the atomic volume relations in a simple way.

the atomic volume curve.¹ Fig 7 has the great disadvantage that it does not show the relations which exist between the main and the sub-groups. It is formed from the table in Fig. 2 by turning each inner loop on a horizontal axis from front to back at its right ends until it falls outside to the right. The atomic volumes of the elements have been plotted against their atomic numbers in Fig. 8. A comparison of Figs. 1, 2, 7 and 8 will show how simply the present form of table expresses the atomic volume relations.

The elements of lowest melting point lie at the left of the table (Figs. 1, 2, and 7). The absolute melting points for these elements are:

Hydrogen.....	14°
Helium.....	2°
Neon.....	20°
Argon.....	85°
Krypton.....	104°
Xenon.....	133°
Niton.....	202°

The line² of highest melting points begins exactly opposite at the right of the outer loop with carbon, melting point about 3900° absolute, and silicon, 1693°. These are the elements of lowest atomic volume except for the fact that the atomic volume of aluminium is slightly less than that of silicon. It might seem that the line of maximum melting point would here jump at once to the elements of lowest atomic volume in the next series, that is, to the iron group. Instead of doing this, however, it passes to titanium (m. p. 2060° Abs.), and then still further toward the eighth group, but reaches only to Group VIB, and passes straight down through molybdenum (2800°), tungsten (3300°), and uranium. The tendency toward the shift of the maximum melting point from the fourth group to Group VIB is already seen in the elements titanium and vanadium. Thus the difference between the melting points of carbon (4th group) and the adjacent element in the fifth group, nitrogen, is 3800°. Between silicon and phosphorus the corresponding drop is 1400°. Just below this the drop from titanium (4th group) to vanadium (Group VB) is only 70°. This enormous decrease in the fall between the fourth and fifth groups, clearly predicts a reversal in the next series, where zirconium (4th group) has a melting point of about 2000° absolute. Columbium (niobium, 5th group) melts at 2500°, and molybdenum (Group VIB) melts at about 2800°.

¹ If the loops at right, representing the sub-groups, are untwisted, this table takes on the form advocated by Emerson in his "Helix Chemica," *Am. Chem. J.*, 45, 160-210 (1911), except that the new table classifies the rare earths in a different way. While this is also a useful form of the table, it has not been thought necessary to include a figure showing it, since it is easy to see how Emerson's table can be modified so as to classify the rare earths correctly.

² For the lines of maximum melting points, and the lines of primary and secondary minima, see Fig. 9.

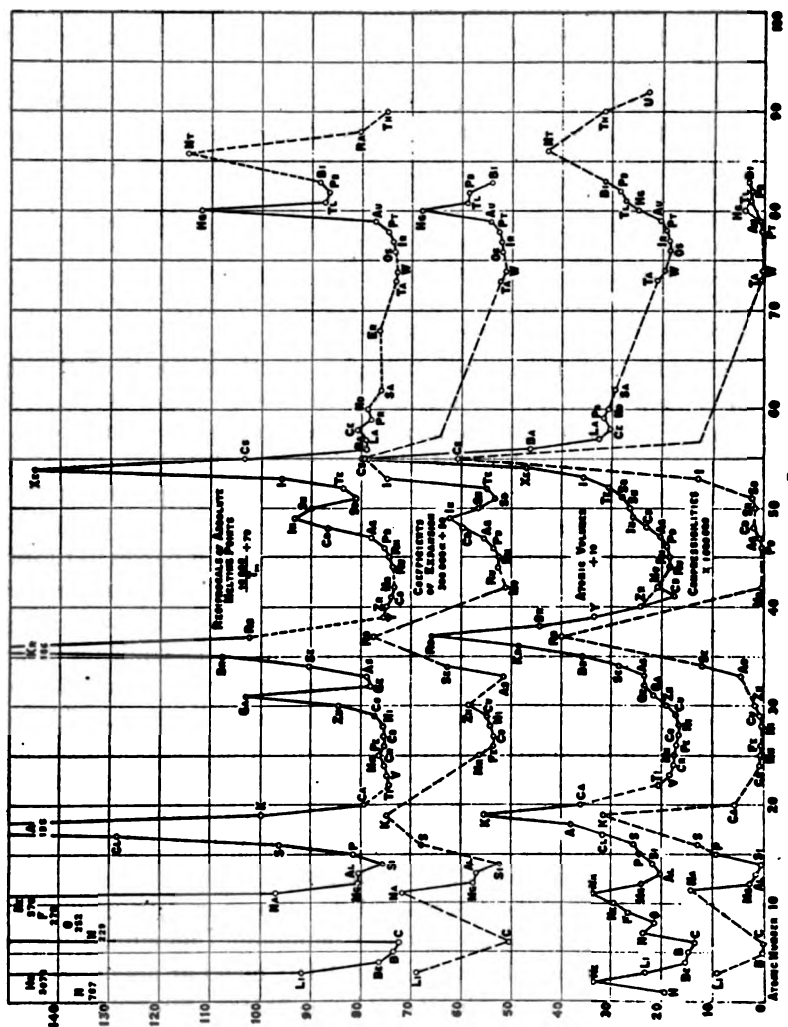
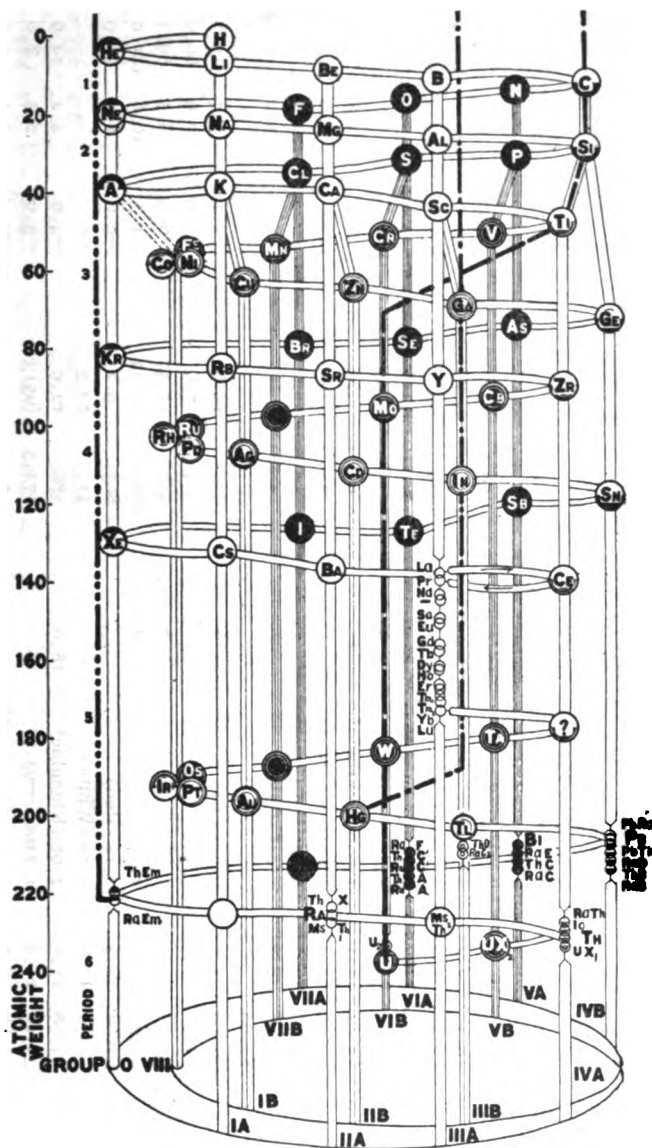


Fig. 8.—Cohesional properties of the elements. (The atomic volume of Cb is probably not correct.)



MELTING POINTS

Line of Maxima _____

Line of Primary Minima.....

Line of Secondary Minima.....

Fig. 9.

TABLE IV.—THE ELEMENTS ARRANGED ACCORDING TO ATOMIC NUMBERS, WITH THE ATOMIC WEIGHTS, ATOMIC VOLUMES, MELTING POINTS, COMPRESSIBILITIES, CUBIC COEFFICIENTS OF EXPANSION, MAGNETIC SUSCEPTIBILITIES, ATOMIC FREQUENCIES, AND VALUES OF T_m/V REPRESENTING COHESION.

At. No.	Element.	At. wt.	At. vol.	Density.	Cubic coeff. of expansion $3\alpha \times 10^4$.	M. p. absolute.	Compressibility at $20^\circ \times 10^4$ (Richards).	Susceptibility $\times 10^7$.	Atomic frequency $\times 10^{11}$.	T_m/V .
1	Hydrogen	1.008	9.2	0.11 ¹ (—252)	...	14	5.5	1.52
2	Helium	4.00	23.5	0.0763 (—259.9)	...	2	0.8	0.085
3	Lithium	6.94	13.1	0.146 (—271.5)	19.0	459	9.0	5.0	10.7	35.0
4	Beryllium	9.1	5.3	1.73 (15)	...	1573	...	—10.0	23.4	296.4
5	Boron	11.0	4.7	2.34	...	2800	0.3	—7.0	29.5	596.0
6	Carbon	12.005	3.4	3.51 (Diamond)	0.3	> 3873	Very small	—4.9	37.0	1139.0
			5.3	2.26 (Graphite)	7.2	...	3.0	—5.21
7	Nitrogen	14.01	13.7	1.0265 (—252.5)	...	63	2.8	4.6
8	Oxygen	16.00	11.2	1.4256 (—252.5)	...	55	...	1160	2.6	4.9
9	Fluorine	19.00	16.7	1.14 (Liq.) (—200)	...	50	2.0	3.0
10	Neon	20.00	19.2	1.04 ³ (Calc.)	...	20(?)	1.2	1.04
		22.00								
11	Sodium	23.00	23.7	0.9725 (o)	21.6	371	15.6	5.1	4.4	15.7
12	Magnesium	24.32	14.0	1.74	7.83	924	2.9	2.6(?)	7.9	66.0
13	Aluminium	27.1	10.4	2.60	7.2	932	1.47	6.0	8.3	89.5
14	Silicon	28.3	11.7	2.42	2.3	1693	0.32	—1.3	10.6	145.0
15	Phosphorus	31.04	14.4	2.15 (Red)	...	863	9.2	—9.0	6.7	60.0
			17.0	1.82 (White)	...	317	20.5
16	Sulfur	32.06	15.5	2.07 (Rhombic)	18.0	386	12.9	—4.9	4.4	24.9
17	Chlorine	35.46	21.4	1.7106 (—93.7)	...	171.5	(95) (?)	—5.90	2.5	8.0
18	Argon	39.88	28.0	1.423 (Liq.) (—189)	...	85	...	—500 (?)	1.5	3.0
19	Potassium	39.10	45.5	0.859 (o)	25.0	335	31.7	0.58	2.6	7.3
20	Calcium	40.07	26.2	1.53	...	1083	5.7	11.0	5.4	41.5
21	Scandium	44.1

22	Titanium	48.1	10.7	4.50 ¹ 3.988 ⁴	...	2063	...	12.4	9.2	193.0
23	Vanadium	51.0	8.5	5.987 ⁴	...	1993	...	15.0	9.5	234.0
24	Chromium	52.0	7.4	7.06	...	1793	0.9	29.0	9.5	242.0
25	Manganese	54.93	7.5	7.37	6.2	1533	0.84	89.3	8.4	204.0
26	Iron	55.84	7.1	7.85	3.6	1803	0.60	...	9.2	254.0
27	Cobalt	58.97	6.7	8.8	3.8	1751	9.0	262.0
28	Nickel	58.68	6.7	8.7	4.2	1725	0.43	...	8.9	258.0
29	Copper	63.57	7.1	8.92	5.0	1356	0.75	—0.85	7.5	191.3
30	Zinc	65.37	9.2	7.13	8.7	692	1.7	—1.55	4.8	75.4
31	Gallium	69.9	11.8	5.92	...	303	...	—2.4	2.8	25.7
32	Germanium	72.5	13.3	5.459	...	1231	...	—1.2	5.4	92.6
33	Arsenic	74.96	13.1	5.72 (Metal) 4.64 (Gray) ⁴	1.6	1123	4.5	—0.1	5.1	85.8
34	Selenium	79.2	16.5	4.8 (Gray)
35	Bromine	79.92	25.6	3.12 (Liq.) (20)	11.4	490-3	12.00	—3.2	3.0	29.7
36	Krypton	82.92	38.5	2.135 (Liq.) (—146)	...	266	52	—3.99	1.9	10.4
37	Rubidium	85.45	56.0	1.5248 (o)	...	104	1.0	2.8
38	Strontium	87.63	34.4	2.55	27.0	311	40	0.7	1.6	5.6
39	Yttrium	88.7	23.3	3.80	...	> Ca < Ba?		—2.0	3.4	...
40	Zirconium	90.6	14.2	6.40	...	1773(?)	4.3	76.2
41	Columbium	93.5	7.4	12.7 ⁷ 8.40	...	1973	...	—4.5	6.0	138.8
					...	2473(?)	8.2	334.0

¹ Occluded in wood charcoal. *Tables Annuelles*, 1913.² *Z. physik. Chem.*, 76, 570 (1911).³ Crystalline. *This Journal*, 32, 336 (1910).⁴ Amorphous. *Tables Annuelles*, 1912.⁵ *Tables Annuelles*, 1914; *Z. anorg. Chem.*, 79, 221.⁶ Liebig's Ann., 361, 1 (1908).⁷ *Landolt-Börnstein-Meyerhoffer Tabellen*. The values for columbium vary greatly, and there is a need for a new determination of the density of the pure substance.

TABLE IV (continued).

At. No.	Element.	At. wt.	At. vol.	Density.	Cubic coeff. of expansion $3\alpha \times 10^4$.	M. P. absolute.	Compressibility at $20^\circ \times 10^4$. (Richards.)	Susceptibility $\times 10^4$.	Atomic frequency $\times 10^{12}$.	T_m/V .
42	Molybdenum	96.0	10.7	7.37	1.1	2773	0.46	0.39	7.6	259.6
43	Eka-manganese I	7.03
44	Ruthenium	101.7	8.4	12.063	2.88	2573	7.7	306.4
45	Rhodium	102.9	8.5	12.1	2.55	2213	...	4.3	7.0	260.6
46	Palladium	106.7	8.8	12.13	3.8	1822	0.54	11.0	6.2	207.0
47	Silver	107.88	10.3	10.5	5.7	1234	1.01	52.0	4.8	120.0
48	Cadmium	112.40	13.1	8.6	9.3	594	2.1	-2.0	3.2	45.3
49	Indium	114.8	15.8	7.277	12.5	428	...	-1.8	2.3	27.1
50	Tin	118.7	16.3	7.29	6.7	505	1.9	-0.2	2.5	31.0
51	Antimony	120.2	17.9	6.71	3.3	903	2.4	-8.2	3.2	50.4
52	Tellurium	127.5	20.5	6.218	5.0	725	...	-3.2	2.7	35.4
53	Iodine	126.92	25.7	4.94	25.0	386	13.0	-3.6	1.8	15.0
54	Xenon	130.2	37.0	3.52 (liq.) (-102)	...	133	0.9	3.6
55	Caesium	132.81	69.8	1.9029 (o)	29	299	61.0	-1.0	1.1	4.3
56	Barium	137.37	36.3	3.78	...	1123	...	-9.0	2.6	30.8
57	Lanthanum	139.0	22.6	6.15	...	1083(?)	3.1	48.0
58	Cerium	140.25	20.3	6.92	...	913	...	150	2.9	44.9
59	Praseodymium	140.9	21.8	6.47	...	1213(?)	...	250	3.2	55.7
60	Neodymium	144.3	20.7	6.96	...	1113(?)	...	360	3.1	53.8
61	Eka-neodymium
62	Samarium	150.4	19.5	7.7	...	1573-1673	3.8	82.0
63	Europium	152.0
64	Gadolinium	157.3
65	Terbium	159.2
66	Dysprosium	162.5
67	Holmium	163.5

68	Erbium	167.7	35.3(?)	4.77(?)	...	1923(?)	...	323.0
69	Thulium I	168.5
70	Thulium II
71	Ytterbium	173.5
72	Lutecium	175.0	Very high
73	Tantalum	111.5	10.9	16.67	2.3	3123	0.53	8.0	7.4	286
74	Tungsten	184.0	9.7	19.23	1.1	3300	0.27	2.2	6.2	340
75.	Eka-manganese
76	Osmium	190.9	8.5	22.48	2.0	2973(?)	...	0.4	6.0	350
77	Iridium	193.1	8.6	22.4	1.97	2573(?)	...	1.3	5.5	300
78	Platinum	195.2	9.1	21.31	2.7	2028	0.38	8.0	4.8	223
79	Gold	197.2	10.3	19.24	4.29	1356	0.64	-1.5	3.7	129.4
80	Mercury	200.6	14.8	13.55 (20)	18.2 (Liq.)	234	3.95	-1.9	1.4	15.8
81	Thallium	204.0	17.2	11.83	9.0	575	2.3	-2.4	2.0	33.4
82	Lead	207.20	18.2	11.37	8.79	600	2.33	-1.2	2.0	33.0
83	Bismuth	208.0	21.2	9.80	4.03	544	3.0	-14.0	1.8	25.7
84	Polonium	210.0
85	Eka-iodine
86	Niton	222.4	39.0	5.7 (Liq.) (-71)	...	202	0.9	5.2
87	Eka-caesium
88	Radium	226.0	973
89	Actinium
90	Thorium	232.4	21.2	11.00	...	> 1973(?) < Pt	...	0.8	3.3
91	Uranium X ₂	234.2
92	Uranium	238.2	12.7	18.7	...	(?)	...	26.0

The unknown element eka-manganese 2 may prove to have a higher melting point than tungsten. The drop in melting point between carbon, atomic number 6, and nitrogen, atomic number 7, is the most remarkable sharp change in the whole system, amounting as it does to more than 3800° . It will be shown later that the relations of the physical properties of carbon to those of the other elements, are remarkable in many other respects.

In addition to the line of minimum melting points, which lies in the zero group, there is a line of secondary minima, possibly beginning with aluminium, with a very slight minimum. The next element in the third group below this is scandium, and unfortunately its melting point is not known. Below this in Group IIIA there is a very considerable minimum beginning with gallium (at. no. 31) of absolute melting point 303° , while just before it zinc (at. no. 30) has a melting point of 692° , and just after it comes germanium (at. no. 32) with a melting point of 1231° . Below gallium the minimum continues in the same group, IIIB, with indium (m. p. 480°), and then shifts to the left (Fig. 9) toward the iron group, so that the next minimum comes in Group IIB with mercury. Here it is remarkable that the secondary minimum where mercury melts at 234° absolute, is almost as low as the corresponding primary minimum at niton, which melts at 202° , or only 32° lower. It will be seen that the line of maximum melting points at the back of the inner loop, and the line of secondary minima at the front of the inner loop, both move to the left toward the iron group as they move down the table. In Fig. 8 the melting points have been plotted as reciprocals, and these secondary minima may be seen as secondary maxima on the curve.

Fig. 8 is similar to a figure given by Richards,¹ but differs in the fact that it is plotted to atomic numbers instead of atomic weights, and also gives data for some of the properties of as many as 72 elements, while Richards' figure shows only 38. The increase in the number of data changes not only the form of individual curves, but it also changes their relationship to each other. When so many data are plotted, there is a considerable advantage in plotting to atomic numbers instead of atomic weights, since when the atomic weights are plotted, each curve is apt to cross itself whenever the atomic weights are not in the order of the atomic numbers, as is the case with argon. Another point in favor of plotting these physical properties according to the atomic numbers instead of atomic weights, is, as will be shown later, that it is the number of external electrons in the atom, and the number of these runs in the same order as the atomic numbers, which, in all probability, determines the cohesional properties of the elements. Moseley's work seems to indicate that the atomic number and the nuclear charge, pre-

¹ THIS JOURNAL, 37, 1649 (1915).

sumably equal to the number of external electrons, are expressed by the same number.

The data on compressibility given in Table IV, and plotted in Fig. 8, have been taken from Richards' work, and the other data were obtained from what seemed to be the most reliable sources, though in many cases there is considerable doubt as to which work is the most trustworthy. A few of the data plotted have been taken from work on liquids, but wherever this is done the fact is specified in Table IV. A dotted line in the figure indicates that data are not available for the elements along the line, while an unbroken line shows that no data have been omitted.

The four curves representing the reciprocals of absolute melting points, coefficients of expansion, atomic volumes, and compressibilities, have all the same form, though they are not so closely similar as those plotted by Richards. The deviations have been introduced by the addition of more data. The two curves at the top, giving the reciprocals of the melting points and coefficients of expansion,¹ are almost exactly similar where the data are complete. Thus the secondary minima in the melting points have corresponding maxima in the coefficients of expansion for indium and mercury, and a maximum may be predicted for gallium, though no determination has been made for this metal. The atomic volume curve does not show any corresponding maxima, and they seem also to be absent from the compressibility curve, though not all of them are known in the latter case.

The only minimum melting point which exactly corresponds to a maximum atomic volume, is that for helium. Below this in the table (Figs. 1 and 8), the maximum atomic volume shifts one group to the alkalis, while the minimum melting point continues to remain in the zero group. In a very similar way carbon is the only element of minimum atomic volume which has the maximum melting point. In the next series the maximum melting point again comes in the fourth group with silicon, but the minimum atomic volume has shifted one group to aluminium in Group III. In the next period molybdenum has the highest melting point, but the element of lowest atomic volume is either ruthenium or columbium, the latter if the density used is correct, but as to this there seems to be considerable doubt, so the minimum is probably at ruthenium. In the next period osmium has the lowest atomic volume, while tungsten with an atomic number two less, has the highest melting point.

To a considerable extent,² the rule holds that elements of low characteristic valence have low melting points, high atomic volumes, high co-

¹ In the figure this curve seems to have much flatter maxima than the one above it, but this is mostly due to the fact that the maxima, which lie in the helium group, are omitted from this curve on account of the absence of data.

² This is not a true, but only an apparent relation, as is shown later.

efficients of expansion, and high compressibility. On the other hand, to the same extent, elements of high maximum characteristic valence have low atomic volumes, small coefficients of expansion, small compressibilities, and high melting points. Blom¹ has calculated a quantity, W , which he finds to have the dimensions of a cohesion. His equation for W is

$$W = \text{constant} \frac{\nu^2 \cdot A}{V^{1/2}}$$

where ν is the frequency calculated from the specific heats, A is the atomic weight, and V is the atomic volume. The curve for $\log W$ has the general form of the melting point curve, and the reciprocal of this curve would therefore have the general form of those plotted in Fig. 6. In other words, the four properties plotted in Fig. 6 are closely related to the cohesion, or it may be considered that the cohesion, or the attraction between the particles, conditions all of the other four properties. The point at which the parallelism between *valence* and *cohesion* meets its worst failure is in the case of the sub-group elements such as copper and zinc, which fall just beyond the eighth group, since the valence of these elements is low and their cohesion high. Therefore a better rule than the above is that in Fig. 2 the elements at the ends of the PERIODS He, Ne, Ar, Kr, Xe, Rn, are elements of high atomic volume, high coefficients of expansion, high compressibilities, low cohesion, and low melting points, while the elements at the middle of the short and long periods, and around the eighth group near the middle of the very long period, are in general the elements of high cohesion and melting points, and low atomic volumes, compressibilities, and coefficients of expansion.

There is also, as might be expected, a general relation between the hardness of an element and the properties under discussion. Thus, the very hard elements lie near the middle of the PERIODS while the softest elements lie near the ends of the periods.

From the above considerations it seems likely that the apparent connection between maximum characteristic valence and cohesion, which however fails so badly in the case of elements of low valence on the inner loop, is not real, but that the *cohesion* is conditioned by the spacing of *all* the electrons of the atom external to the nucleus, and that this spacing is a periodic function varying in the *periods* corresponding to those given in Fig. 2. On the other hand, the *valence* varies in *SERIES*, and only partly according to the periods. Thus the valences 1, 2, 3, 4, 5, 6, 7 depend only on the position in the series; and only the occurrence of the two valences 0 and 8 depends upon the position in the periods.

It seems probable that the atom is a system consisting of a positive nucleus, surrounded by one or more negative electrons which are describing

¹ *Ann. Physik*, [4] 42, 1397-1416 (1913).

orbits at a high speed. It is not improbable that the force which keeps two atoms apart is due to the repulsion of the negative electrons of one atom for those of the other. The compression of a solid would bring these atoms closer together and the closer approach of the external electrons would rapidly increase the repulsion. The principal decrease in volume, is, in all probability, most largely due to the decrease in distance between the atoms. When such large pressures as those used by Bridgeman are used, it would seem likely that there may be a considerable decrease in the size of the atoms themselves. That the atoms are compressible would seem almost certain, but the possibility exists that the atoms may be very much less compressible than the spaces around them.

The Dimensions of Atoms.

It is of interest in this connection to compare what are often called atomic diameters, but which are more properly considered as the distances between the centers of two atoms in a gas during a collision, as determined from the kinetic theory, and the distances between the centers of the same atoms in their positions of equilibrium in the solid or liquid state. Such a comparison is given in Table V.

TABLE V.—ATOMIC DIAMETERS OF MONATOMIC GASES (DISTANCE BETWEEN ATOMIC CENTERS DURING COLLISION) AS DETERMINED FROM THE KINETIC THEORY, AND THE DISTANCES BETWEEN THE CENTERS OF THE ATOMS IN LIQUIDS OR SOLIDS.

Substance.	Number of external electrons.	Atomic diameter $\times 10^8$ cm. in gases at 0° C. = D.	Distance $\times 10^8$ cm. between centers of atoms in solids or liquids.	T_m/V .
			3.38 (—258° adsorbed in charcoal)	
He.....	2	1.7	3.94 (—271.5°)	0.085
Ne.....	10	2.1	3.17 (calc.)	1.04
A.....	18	2.5	3.56 (Liq., —189°)	3.0
Xe.....	54	3.2	3.94 (Liq., —102°)	3.6
Molecular Diameters of Diatomic Gases.				
H ₂		2.1	3.12 (—252°)	
N ₂		2.8	3.56 (—252.5°, solid)	
O ₂		2.6	3.33 (—252.5°, solid)	

At first sight it might seem that the data on the distance between the centers of the atoms in gases during collisions could be explained on the basis that the lighter atoms approach each other more closely because they have the greater velocities, but that this is not true can be seen when it is remembered that the heavier atoms have the greater momentum, so the closer approach of the lighter atoms of the helium group is due to the fact that either (1) the atoms are smaller, or (2) that the fields of force around them are less intense on account of the fact that they have a smaller number of electrons external to the nucleus (as well as a higher nuclear charge). Probably each of these factors plays a part. Thus if the number of external electrons is equal to the

nuclear charge, and we use the hypothesis that the nuclear charge is equal to the atomic number, then it might reasonably be expected that the 54 external electrons of xenon would both occupy more space, and create a more intense field of force than the 2 external electrons of helium. If the number of external electrons is indicated by N , then $\frac{N_{\text{Xe}}^{1/5}}{N_{\text{He}}^{1/5}} = 3$, so that if the distances between the centers of like atoms during collision were proportional to the cube root of the number of external electrons, then since this distance D is 1.7 for helium it would be 5.1 for xenon, while the calculated value is less than this, or 3.2. However, the momentum of the xenon atom is 5.7 that of the helium atom, so that the higher momentum would cause the atoms to approach closer than a distance of 5.1, but it is doubtful if even a momentum 5.7 times as great would be able to reduce D to 3.2. In Table VA, values are given for different roots of N , the momentum, and the calculated values of D from Table V.

TABLE VA.

Atom.	Relative momentum.	$D \times 10^8 \text{ cm.}^1$	$hN^{1/5}$	$hN^{1/4}$	$hN^{1/3}$	N .
He.....	1.0	1.7	1.7	1.7	1.7	2
Ne.....	2.2	2.1	2.3	2.5	2.9	10
A.....	3.15	2.5	2.6	2.9	3.5	18
Xe.....	5.7	3.2	3.3	3.9	5.1	54

The table shows that the distance of approach D varies quite closely as the fifth root of the number of external electrons N . If all of the atoms at 0° had the same momentum this might be thought to be the law which conditions their approach, but since the momentum increases rapidly with the mass of the atom, it is probable that D would vary more nearly as the fourth or third root if the momenta were the same. That D is found to vary as the fifth root of N , when the momentum is involved in addition to the number of external electrons N , is probably due to the fact that the momentum is a function of the atomic weight, which is a function of the atomic number, or N , in this case the number of charges

¹ The values of D are taken from Landolt-Börnstein-Meyerhoffer *Tabellen* and are calculated from the equation $D = \sqrt{\frac{350 \rho \bar{c}}{\sqrt{2} \pi n \mu}}$, where n is the number of molecules per cc. at 0° and 760 mm. Hg $= 2.705 \times 10^{19} \text{ cm.}^{-3}$, and μ is the viscosity of the gas, with the application of Sutherland's correction for cohesion force (*Phil. Mag.*, 17, 320 (1904)), and Jean's correction for the persistence of velocities. The constants involved in this calculation are not very well known, and may vary for different kinds of atoms, but are probably the same for atoms of the same kind, such as those of the helium group. In a table prepared by the General Electric Company the values of D are given as follows: He = 1.905, A = 2.876, and these numbers are in the same ratio as those given by Landolt-Börnstein. On account of the uncertainty in the constants, it has not been thought worth while to recalculate the numbers, since the relative values would not be affected.

on the nucleus. In other words the various factors involved are functions of the same variable.

If the heavier helium group atoms are larger it may seem surprising that in the liquid state the distance between the atomic centers is practically the same, but this is due to the fact, as is shown by the last column in Table V, that the cohesion increases very rapidly with the atomic number. At present little is known as to the actual dimensions of atoms, and it seems probable that their dimensions are smaller, rather than larger than those usually cited. It is somewhat difficult to know what is meant by the atomic diameter, since in a simple atom, such as hydrogen, it might be expected that the diameters would be very different in the different directions.

In the calculation the number of gram molecules per gram molecular weight was taken as 6.062×10^{23} . According to the table the centers of the atoms in liquids or solids are much farther apart than the distance between the centers in gases at the time of their closest approach during collision. Even in their collisions it is improbable that the exterior electrons come very closely in contact in comparison with their dimensions. The data in Table V are in accord with the usual assumption that a large part of the space in liquids and solids is outside the boundaries of the atoms, though the interatomic spaces are certainly regions in which the electro-static and electro-magnetic forces are intense.

Atomic Frequencies.

The properties of the elements which have been considered thus far are properties of the atoms in bulk, undoubtedly conditioned however, by the structure of the single atoms. An endeavor has been made to find some property which is more characteristic of the atoms themselves. This attempt has met with success in the discovery that the atoms of solid substances have characteristic atomic frequencies. While in the simple theory the atomic frequency may be considered as independent of the nature of the substance, this is not altogether true, since, for example, there is found to be a difference in the values obtained for diamond and graphite. On the other hand, it is remarkable, as has been pointed out by Nernst, that the frequencies of sodium atoms in metallic sodium and in sodium chloride, though not exactly, are approximately the same, so as a first approximation the atomic frequencies may be considered as a property of the atom.

The characteristic equation for the frequency is the formula for the simple pendulum

$$\nu = \frac{1}{2\pi} \sqrt{\frac{D}{A}}$$

where A is the atomic weight, and D is the directional force. The frequencies for the different atoms are given in Table II, and in Fig. 10.

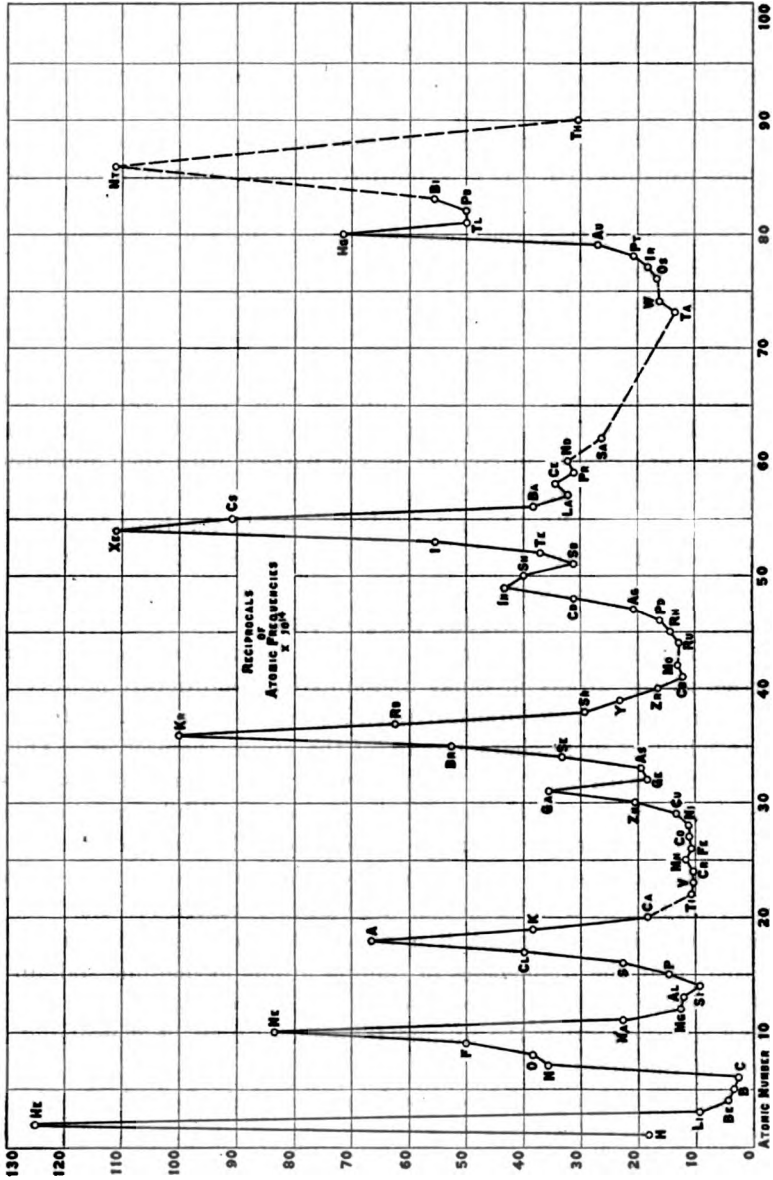


Fig. 10.

However, in the figure the reciprocals of the frequencies have been plotted instead of the values themselves, since the change makes the curve comparable with those representing the atomic volumes, compressibilities, coefficients of expansion, and reciprocals of the melting points, as plotted in Fig. 8.

The different equations which may be used for the calculation of ν have been discussed by Blom,¹ who has compared them and finds that no one is exclusively better than the others. The equations are given below, where the symbols have the following meanings:

T_m = absolute melting point.

d = density.

V = atomic weight.

K = compressibility.

α = linear coefficient of expansion.

C_p and C_v = atomic heats.

1. Einstein's equation.²

$$D = \text{const.} \frac{V^{1/2}}{K}.$$

$$\nu = 3.3 \times 10^7 \cdot A^{-1/2} \cdot d^{-1/2} \cdot K^{-1/2}.$$

2. Lindemann's equation,³ derived from the hypothesis that at the melting point the orbits of the atoms become just large enough so that the atoms come into direct contact, and that on account of the consequent energy exchange between the atoms, they are no longer able to hold to their positions relative to the space lattice, but begin to slide past each other.

$$D = \text{const.} \frac{T_m}{V^{2/3}}.$$

$$\nu = 3.1 \times 10^{12} \cdot \sqrt{\frac{T_m}{A \cdot V^{2/3}}}.$$

3. Alterthum,⁴ from dimensional considerations, found the following:

$$D = \text{const.} \frac{1}{\alpha V^{2/3}}.$$

$$\nu = 4.2 \times 10^{11} \sqrt{\frac{1}{A \alpha V^{2/3}}}.$$

4. Benedicks⁵ considered D as proportional to the internal pressure of the solid as determined by van der Waal's equation.

$$D = \text{const.} \frac{R}{3\alpha V}.$$

¹ *Ann. Physik*, 42, 1397-1416.

² *Ibid.*, 34, 170 (1911); 35, 679 (1911).

³ *Inaug. diss., Berlin*, 1911; *Physik. Z.*, 11, 609-12 (1910).

⁴ *Verh. deutsch. physik. Ges.*, 15, 68 (1913).

⁵ Benedicks, *Ann. Physik*, 42, 154 (1913).

$$\nu = 6.3 \times 10^{11} \sqrt{\frac{d}{\alpha}}.$$

5. Grüneisen's¹ equation:

$$D = \text{const.} \frac{C_p}{3\alpha V^{2/3}},$$

$$\nu = 2.9 \times 10^{11} \sqrt{\frac{C_p}{3\alpha V^{2/3}}} \text{ (gr. cal.)}.$$

6. Debye's well known equation is

$$\nu = 7.4 \times 10^7 A^{-1/3} d^{-1/3} K^{-1/3} f(0)^{-1/3},$$

where $f(0)$ is a function of Poisson's constant. Debye considers ν to have a maximum value, which is the one given by the equation. The other authorities cited consider ν to have only one value under definite conditions. Blom finds, however, that the more exact equation of Debye does not give better values, since the data involved are not so good as those required by some of the other equations.

Of all the equations given, only that of Lindemann can be used if a comparison including nearly all of the elements is desired, so this method of calculation has been chosen for the data plotted in Fig. 8. About half of the values have been calculated from those given by Biltz,² who used a different constant, and the rest have been calculated from the other data given in Table II.

The figure shows that the curve has a considerable resemblance to that giving the reciprocals of the melting points (Fig. 6). The greatest minimum in atomic frequencies (maximum on the curve) comes at helium, lesser minima at neon and argon, and then greater minima at krypton, xenon and niton. The secondary minima come at gallium, indium, mercury, just as in the melting point curve. The maxima occur at carbon, silicon, titanium to nickel, columbium to ruthenium, tantalum, and thorium (U), with minor maxima at germanium, antimony, and thallium to lead.

As has been pointed out by Biltz, carbon, which forms the greatest number of compounds of any of the elements, many of them very complex, has by far the highest atomic frequency (37.0), and silicon, which does the same to a lesser degree, is also at a peak in the frequency curve, but with a value only about one-third of that of carbon. The elements which form a large number of complex ammonia compounds, occur at maxima in the frequency curve (minima in the reciprocal curve). Such elements are chromium, cobalt, platinum, etc. Further, elements just to the right of these maxima, on descending branches of the frequency curve, also form these complexes. Beryllium, which forms very stable

¹ Grüneisen, *Ann. Physik*, 39, 293 (1912).

² *Z. Elektrochem.*, 17, 170-4 (1911).

hexamines, has a very high frequency, equal to 23.4. The fact that on the curve hydrogen has the same relative position as the halogens, is taken by Biltz¹ to indicate that it belongs to the halogen group, but this does not prove the point, since in chemical behavior hydrogen is not like the halogens. A study of the frequency curve will reveal many other relations which cannot be discussed here.

According to Equations 1, 2, 3 and 5, the following quantities must be proportional to each other:

$$\frac{1}{K}, \frac{T_m}{V}, \frac{R}{3\alpha V}, \text{ and } \frac{C_p}{3\alpha V}$$

Blom¹ considers that these represent the *cohesion pressure*. He plots the logarithm of this cohesion pressure for each of these functions, and all of the curves have exactly the general form which the curve of the reciprocals of the atomic frequencies would have (Fig. 8) if it were inverted. A comparison of the above functions shows the relationships which exist. Thus from (2) and (3) $T_m = \text{const. } \alpha$ and from (2) and (5) $T_m \sim C_p/\alpha$. A number of these relations have been studied by Grüneisen.² From (1) and (2) it may be found that $K = \text{const. } V/T_m$. Richards finds empirically that this relation does not contain the density to a high enough power, and that the expression $K = \text{const. } \frac{A}{D^{1.25}(T_m - 50)}$ is much more exact. In order to correspond more closely to the above expressions Richards' equation should be put in the form $K = \text{const. } \frac{V}{(T_m - 50) D^{0.25}}$.

This equation may be interpreted to mean that the compressibility varies not only as the atomic volume, and as the reciprocal of the melting point, but also as the reciprocal of some function of a quantity which varies very nearly as the density. It is possible that this quantity is the number of external negative electrons in the gram atom divided by the atomic weight, or the number of external negative electrons per unit volume. This may be called the electronic density (d_e). Reasoning from the standpoint of modern theories of atomic structure, there would seem to be no reason why the density of the material itself should enter into the theoretical equation as a modifying factor in addition to its occurrence in the atomic volume, but it is easily apparent that the electronic density might be a factor.

An empirical equation which holds as well as that given by Richards, for the sixteen cases for which he calculates the values,³ and which is simpler, is

¹ *Loc. cit.*

² *Ann. Physik*, 33, 33, 65 (1910); 39, 300 (1912).

³ *THIS JOURNAL*, 37, 1652 (1915).

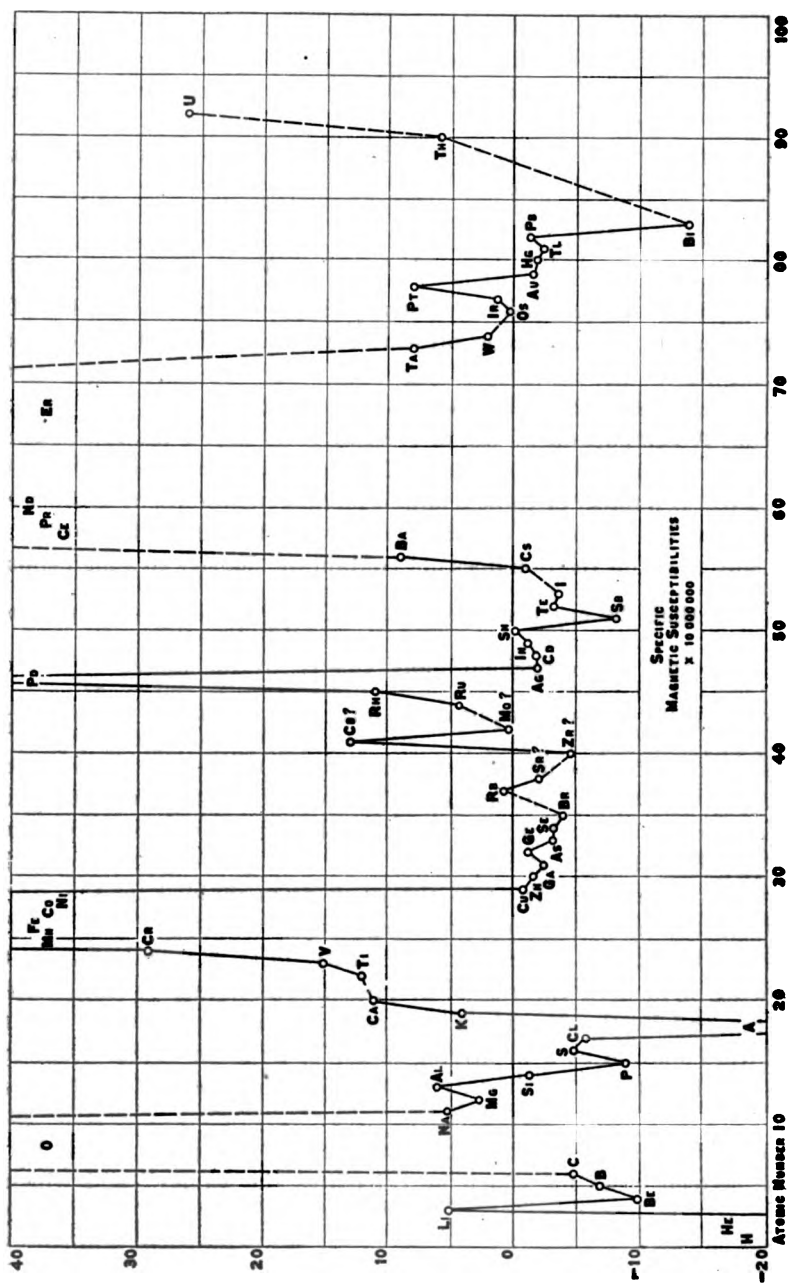


Fig. 11.

$$K = \text{const.} \frac{N}{T_m D^{1.25}}$$

Which equation gives better results in general has not been tested.

Hardness.

The hardness of the elements¹ has been studied by Rydberg, who finds that the curve for hardness has the general form of the melting point curve, or of the curve which represents cohesion (Fig. 12). The minor differences in the two sets of curves are as follows: In the melting point or cohesion curves the line of minor minima runs gallium, indium, mercury, while in Rydberg's curve of hardness it runs gallium, indium, thallium, but this difference between mercury and thallium is probably due to the temperature at which the hardness of the mercury was determined as compared with that at which the thallium was measured. Another point of difference is that chromium stands very much higher in the curve of hardness than in either of the other curves. The data for hardness are very inaccurate, but the conclusion is inevitable that the hardness is proportional to some function of the cohesion. Traube² finds that the hardness and modulus of elasticity also run parallel. Blom³ gives curves for a number of oxides of the type RO, and shows that when the mean atomic heat, the square root of the atomic volume, and the softness (reciprocal of the hardness on Moh's scale) are plotted, as functions of the atomic weights, the three curves have the same form. The same relation is found to hold for oxides of the form R₂O₃.

The Elastic Properties of the Elements.

Johnston⁴ gives tables which show that for the twelve metals which he considers, the hardness, modulus of elasticity (Young's), rigidity, and tenacity, all increase in the same order, and in the order in which the compressibility decreases. A study of the elements as a whole, shows that somewhat the same general relations hold to some extent for elements which are not metals, but the exceptions to the rule are numerous, and the magnitude of the exception is often considerable. The regularity of the behavior of the metals with respect to these properties is remarkable.

Cohesion.

A very simple experiment upon isotopes would give much light as to which part of the atom by its variation in structure or mass, conditions the changes in cohesion. Fig. 12 shows the variation in the values of T_m/V , where T_m is the absolute melting point and V the atomic volume. Blom³ claims that the values of this function represent the cohesion. In the curve the logarithm of the function is plotted, since other-

¹ *Z. physik. Chem.*, 33, 359 (1900).

² *Z. anorg. Chem.*, 34, 420-4 (1903).

³ *Loc. cit.*

⁴ *Z. anorg. Chem.*, 76, 365 and 367 (1912).

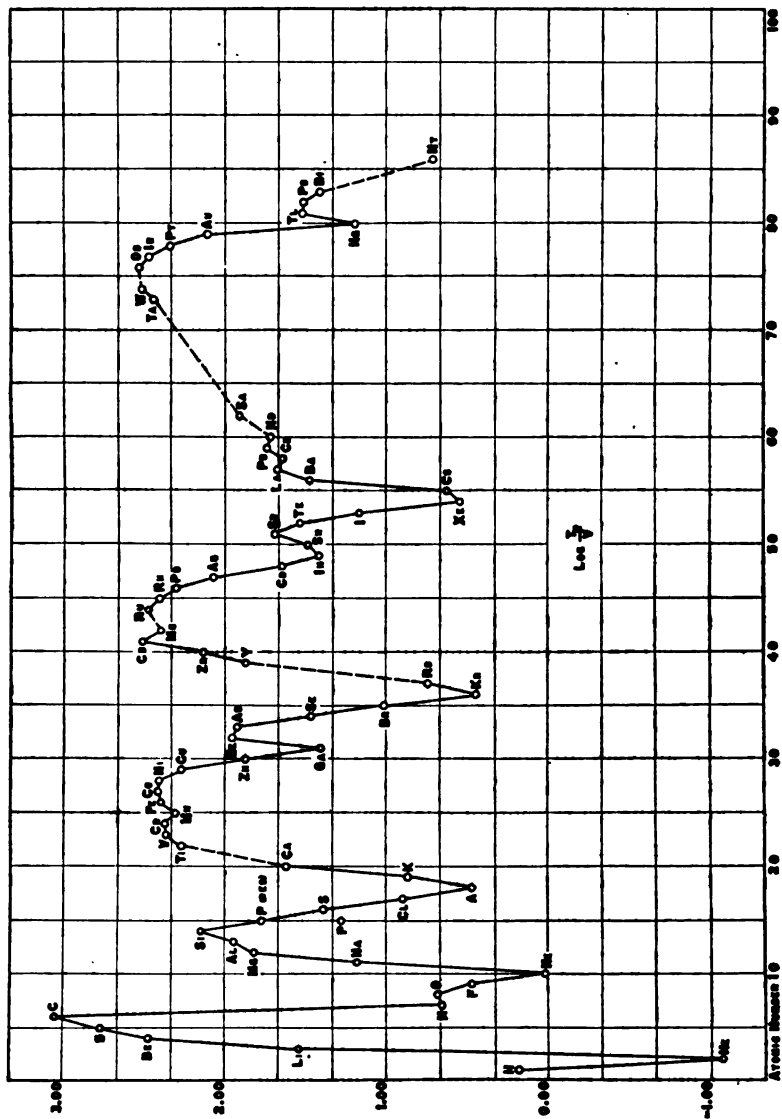


Fig. 12.

wise the curve for the function itself would be difficult to plot on one page. Lindemann¹ proves by thermodynamics, on the basis of certain assumptions, that the melting points of isotopes are proportional to their atomic weights. According to this conclusion lead from thorium should have a melting point about six degrees greater than that of lead from radium. Lindemann's result may be stated as follows in terms of recent atomic theories: Whenever the nuclear charge remains constant the melting point and the cohesion vary as the mass of the nucleus. He concludes, therefore, that "the forces of attraction and repulsion between atoms, the interaction of which results in the solid state, have their origin in the nucleus." Lindemann's calculation, however, involves several doubtful assumptions, so it is not certain that his conclusion is correct, and it may be well to consider the question from another point of view.

Following out his line of reasoning, it could be predicted that if an isotope of carbon, of atomic number six (and possibly of nuclear charge six also) could be obtained with a mass of 14, its melting point would be about 4400° . If this should then undergo a beta change, it would become nitrogen, with a melting point of 63° , or of about one-seventieth the melting point which it had before the loss of the one negative electron from the nucleus. Presumably when the nucleus loses a negative electron, the number of external electrons increases by one in the formation of the neutral atom. If this is true, a change of one electron from the nucleus into an external electron, without a change of mass, would cause this enormous change of melting point amounting to more than 4300° , or of six thousand per cent. when calculated on the basis of the melting point of nitrogen. If Lindemann's idea is on the other hand incorrect, and if isotopes have the same melting points, then it will be seen that the isotope of carbon of mass 14 would have a melting point of about 3800° , and the melting point would be changed about sixtyfold by the change of one electron from the nucleus to the external region. Changes similar to these actually occur among the radioactive elements, but the changes of melting point with these heavier atoms are not so striking. A single beta change (that is the loss of an electron by the nucleus, and the resultant increase of one in the nuclear charge, and probably in the number of external electrons) may decrease the melting point, for example, in the beta change from an isotope of lead to an isotope of bismuth the decrease is 56° , or in another case, such as the beta change of thorium, it may increase the melting point. Thus the great changes of cohesion which occur inside of one period in the periodic system, whether of electrostatic or of electro-magnetic origin, and more probably of both, must depend much more on the arrangement and frequencies of the particles, either in the nucleus, or in the external region of the atom, than they do

¹ *Nature*, 95, 7 (1915).

upon the changes of mass. Thus, in the first period, as the cohesion curve shows, there occur both the lowest minimum and the highest maximum in cohesion in helium and carbon, respectively, elements which differ in atomic mass by only eight. It is evident that such extreme changes would result from differences in arrangement only when the number of electrons is small.

The question under consideration here is not the origin of cohesion, but of its variation with the atomic number. This variation may be caused either by a change in arrangement or frequency in the nucleus, or among the external electrons, but there are several arguments which seem to indicate that it is the external changes which are the important ones, and that it is the external electrons which determine the spacing of the atoms, and therefore the atomic volume. It is evident, of course, that it is the nuclear charge which determines the number of these electrons, and therefore their arrangement. There is a very close relation between the variations of valence in the periodic system, and the variations in cohesion properties. Since the valence is undoubtedly conditioned by electrons external to the nucleus, it is probable that the same is true of the related cohesion properties, but that it is the whole system of external electrons which is effective in the latter case. The nuclei of atoms fall into two series, which differ in stability according as the atomic number is odd or even. This subject will be more fully considered in a later paper, but as to the fact there is no doubt. Now neither the chemical nor the physical properties of the elements show this marked distinction between the odd and even numbered elements, which would seem to indicate that it is not the changes in the nucleus which are here effective. On the other hand, it must be realized that electromagnetic effects caused by the rotation of the nucleus, or of its parts, *may* have an effect upon the arrangement of these external electrons.

The cohesion is not a function of the properties of the atoms alone, but it is also conditioned by the form of the space-lattice in the solid, as is evident if graphite and the diamond are compared.

Magnetic Susceptibility.

In Fig. 11 the susceptibilities of the elements per unit mass times 10^7 have been plotted. Most, but not all, of the data were taken from a paper by M. Owen.¹ The maxima for the elements of positive susceptibility come with oxygen, and then an extremely high maximum in the first eighth group, Fe, Co, and Ni. The next maximum is not nearly so high, but comes in the eighth group again with Pd. After this there is a high maximum in the rare earths, a minor maximum in the eighth group with Pt, and a maximum of moderate height at uranium. It is interesting that the highest maximum is in the eighth group the **FIRST** time it ap-

¹ *Ann. Physik*, [4] 37, 657-99 (1912).

pears in the system, and that the next highest maximum comes with the first and only appearance of the rare earth group. Both of these groups are related to each other in that in them the valence remains constant as the atomic number increases. Neon, *not* determined by Owen, seems to be a minimum on the susceptibility curve. At least this is true if the experimental work is trustworthy. The minima found by Owen are Be, P, Zr, Sb, and Bi. A rough relationship between the atomic volume curve and the susceptibility curve may be seen by bringing the two together, but there are many points of deviation between the two. A plot showing the atomic magnetism would of course greatly exaggerate the deviations from the zero line for elements of high atomic weight.

Fig. 11 is interesting in that it proves conclusively that the old standard rule that elements of the even series are paramagnetic, and that elements of the odd series are diamagnetic, is not *entirely* correct, and that, for example, the susceptibility changes from positive to negative in a single series. The fifth series, however, seems to be entirely negative, as is also the seventh, and the ninth, as far as it is known.

Thus in the short periods there is a change from diamagnetic to paramagnetic in each *series*, but in the long periods beginning with argon, which is strongly diamagnetic, there is a first jump to a slightly paramagnetic substance in potassium. Then in these long periods *the elements on the front of the outer loop and the back of the inner loop are paramagnetic; those on the front of the inner loop and the back of the outer loop are diamagnetic.* Beginning with the long periods, *the iron group elements are the maxima of the paramagnetic elements* (with an additional maximum in the rare earths), and *the maxima of diamagnetism in all probability occur in the zero group elements.* Thus the zero and eighth groups form the two extremes in the curve representing magnetic properties, just as they do with respect to atomic volume, cohesion, and related properties. This suggests that cohesion is partly due to magnetic forces. That it is not the only factor involved is, however, shown by the many deviations between the course of the two sets of curves. Thus carbon, which forms a maximum in the cohesion curve, is very far from the maximum on the susceptibility curve.

The Number of Lines in the Spectrum of an Element.

On pages 36 and 37 of their book "Die Spektren der Elemente bei Normalem Druck," Volume 1, Exner and Haschek give curves showing the relationship between the atomic weight and the number of lines in the spectrum of an element. It is somewhat difficult to see just how they have decided upon the number of lines in each case, as they give only one line for the spark spectrum, and none for the arc spectrum of hydrogen, and only one line for the arc spectrum of carbon. The values of such results depend upon their method of choosing the lines to be counted.

They find that the curve giving the number of lines in the spark spectrum has maxima at V, Mo, W, and U, and this falls very nearly along the line of maximum melting points. Secondary maxima occur at Fe, Nd, Er and Ir. Of all of the elements they find uranium with the heaviest atom and the greatest number of external electrons, to give the most lines.

Complex Compounds of the Periodic System.

It is a well-known fact that the *elements which form the greatest number of compounds*, such as carbon and silicon, *are elements of low atomic volume*. Thus they are elements of high cohesion, and they also have a high valence.

The stability of a particular type of complex compounds has been studied carefully by Ephraim, who measured the temperature at which the vapor pressure of ammonia from complex metal ammonia compounds of the type $MX_3 \cdot 6NH_3$, becomes equal to 500 mm.

TABLE III.—TEMPERATURES AT WHICH THE VAPOR PRESSURES OF HEXAMMINE COMPOUND BECOMES EQUAL TO 500 mm.

Metal.	Atomic volume.	T_m/V .	Dissociation temperatures. Hexammines.	
			Chlorides.	Sulfates.
Be.....	5.3	296.4	High temp.	...
Ni.....	6.7	258.0	165	398
Co.....	6.7	262.0	130	378.5
Fe.....	7.1	254.0	106.5	369
Cu.....	7.1	191.3	95	364.5
Mn.....	7.5	204.0	82	340
Zn.....	9.2	75.4	51	299
Cd.....	13.1	45.3	50.5	323.5
Mg.....	14.0	66	24.5	...
Hg, Sn, Pb.....	> 14	< 42	Do not give comparable compounds at room temperatures.	
Ca, Sr, Ba.....	..			

For any one series investigated, Ephraim¹ finds that the product of the cube root of the atomic volume ($V^{1/3}$) by the cube root of the temperature of decomposition ($T_D^{1/3}$) is practically a constant. In the case of the substituted ammonia compounds, the stability of the ammine seems to depend also upon the molecular volume of the organic base. The nature of the anion influences the stability.

The elements which form complex ammonia compounds belong, mostly, in the inner loop of the periodic table (Figs. 1 and 2) and are sub-group elements. On the whole, the elements at the left of the inner loop form the greatest number of these compounds. That the stability increases as the atomic volume of the metal decreases, is apparent from Table III, though there are some minor exceptions to the rule. Thus cadmium, with an atomic volume of 13.1, seems to form a more stable hexammino-sulfate than zinc, with an atomic volume of 9.2. However, the ammino-

¹ Ber., 45, 1323 (1912); Z. physik. Chem., 81, 513, 539 (1913); 83, 196 (1913).

chlorides of these elements follow the usual rule. The values of T_m/V for the elements which represent the cohesion, seem to be in as close a relation to the dissociation temperatures of the chlorides as the atomic volumes.

Valence and Electroaffinity.

The important subject of the relation between the periodic system and electroaffinity has been so thoroughly treated in the classic papers of Abegg and Bodlander,¹ and Abegg,² that it need not be considered here. It may be pointed out that while in general, in any one group, the positive character of the elements increases as they go down the rod on which they lie in the table, this rule is reversed for those elements which are at the left (iron group) and on the front of the inner loop and for the rare earths. Thus copper, silver and gold are progressively more negative, and the same is true of iron, ruthenium, and osmium, and also of zinc, cadmium, and mercury.

Other Properties of the Elements.

According to Cary Lea,³ the maxima for color in the ions formed by the elements are in the three-eighth groups and in the rare earth group, with a final maximum at uranium. This is interesting in so far as it is true, in that this relationship is similar to that found for the maxima of susceptibility, for in both cases the maxima occur in the groups where the valence remains constant as the atomic number rises.

Other properties of the elements, beside those discussed in this paper, which vary in a more or less regular way with their position in the periodic system, are given in the following list, which, however, is not complete:

Electrical conductivity⁴

Conductivity for heat

Boiling points⁶

Heats of chemical combination^{6,7}

Electrode potentials⁷

Changes of volume on fusion⁸

Solubility⁹

Latent heat of fusion¹⁰

¹ L. Abegg, "Die Valenz und das periodische System Versuch einer Theorie der Molekularverbindungen," *Z. anorg. Chem.*, **39**, 330-80 (1904).

² Abegg and Bodlander, *Ibid.*, **20**, 453-99.

³ *Chem. News*, **73**, 203, 260-2 (1896); *Z. anorg. Chem.*, **9**, 312-28 (1895); *Am. J. Sci.*, [3] **49**, 357 (1895).

⁴ Sander, *Elektrochem. Z.*, **6**, 133.

⁵ Carnelley, Numerous papers in *Trans. Chem. Soc., Proc. Roy. Soc. and Phil. Mag.*, from 1876 on.

⁶ Laurie, *Phil. Mag.*, [5] **15**, 42 (1883); Richards, *Trans. Chem. Soc.*, **99**, 1201 (1911); Carnelley, *Phil. Mag.*, [5] **18**, 1-22 (1884).

⁷ Abegg, *Z. anorg. Chem.*, **39**, 330-80 (1904).

⁸ Topler, *Wied. Ann.*, **53**, 343 (1894).

⁹ Abegg and Bodlander, *Am. Chem. J.*, **28**, 220-8 (1902); Locke, *Am. Chem. J.*, **20**, 581-92 (1898); **26**, 166-85, 332-45 (1901); **27**, 455-81 (1902).

¹⁰ Rudorf, "Das Periodische Gesetz," pp. 143-9.

Ionic mobilities¹
 Ultraviolet vibration frequencies²

Refractive indices³
 Spectra³
 Mechanical properties⁴

Summary.

1. In this paper a periodic table has been presented, which shows graphically the relations between the main and the sub-groups of elements. The main defect of the periodic tables which have been designed formerly, is that they do not show these relations correctly.

2. The table arranges the elements in the exact order of their atomic numbers, and gives no blanks for unknown elements which do not correspond to atomic numbers as determined by Moseley's work on the X-ray spectroscopy of the elements.

3. It also plots the elements according to their atomic weights, so the isotopic forms of an element may be shown graphically on the table, and the alpha and beta decompositions of the radioactive elements may also be plainly depicted.

4. Both the zero and the eighth groups fit naturally into the system.

5. The table may be best represented as a helix in space, but may be shown as a spiral in a plane. The space form is represented by its vertical projection on a plane, but drawn with line perspective so that it may easily be visualized.

6. Beginning at the zero group, the maximum positive valence of a group is found by counting toward the front and toward the right, Li = 1, Be = 2, etc., and negative valence by counting toward the back, Fe = -1, O = -2, N = -3, etc.

7. The elements in the table divide themselves into cycles,

Cycle 0
 Cycle 1 = 4² elements
 Cycle 2 = 6² elements
 Cycle 3 = 8² elements

but the latter part of the third cycle is missing. The cycles are each divided into two periods. The periods are as follows:

Period O₁
 Period O₂
 Period 1 = 2×2^1
 $2 = 2 \times 2^1$
 $3 = 2 \times 3^1$
 $4 = 2 \times 3^1$
 $5 = 2 \times 4^1$
 $6 = 2 \times 4^1$

¹ Bredig, *Z. physik. Chem.*, 13, 289 (1894).

² *Ibid.*, 149-57; Bishop, *Am. Chem. J.*, 35, 84 (1906).

³ *Ibid.*, 157-171; Baly, "Spectroscopy."

⁴ *Ibid.*, 187-96.

⁵ Byk, *Ann. Physik*, [4] 42, 1417-53 (1913).

These relations are undoubtedly a numerical expression of a function connected in some way with the system according to which the nuclei of the elements have been built up.

8. Whenever the valence drops, in passing along the continuous line connecting the elements in the order of their atomic numbers, it always drops by seven, either from seven to zero, or from eight to one. In the latter case there is evidenced a certain sluggishness in the drop, so that it is not entirely complete, so that copper, silver and gold, the members of which should have the maximum valence one, often exhibits a higher valency, such as two for copper and three for gold.

9. The table arranges the groups into 5 divisions, numbered 0, 1, 2,

3, 4. These divisions comprise the following groups:

Division.....	0	1	2	3	4
Groups.....	0.8	1.7	2.6	3.5	4.4

The two groups of one division are said to be complementary. The sum of the group numbers of two complementary groups is always 8, as is also the sum of the maximum valences. The algebraic sum of their *characteristic* valences is, on the other hand, always zero. Thus the characteristic valence for Group 1 is +1, and for Group 7 is -1. The characteristic valence of the eighth group needs to be defined in this sense, and must be taken as -0, which accords with Abegg's valence system.

10. Another very important relationship given graphically in this table, and not at all by any other which the writers have found, is that between the main and the sub-groups in any one division. Whenever the group numbers in any one division differ considerably, as is the case in divisions 0 and 1, then the elements in the sub-groups are quite different chemically from the members of the main group, although they are in general alike in valence. As the group numbers in the division approach each other in magnitude, the elements of the sub-group become chemically much like those of the main group. This is true of groups 4A and B, where the group numbers are the same, and the two groups are practically indistinguishable in their general chemical nature.

11. On the outer cylinder the main Groups 1, 2, 3 become LESS positive as the group number increases, while the corresponding sub-groups become MORE positive.

12. Whenever the atomic volume of a main-group element is large, that of the corresponding sub-group element is small, and as the atomic volume of the main group element decreases, that of the sub-group increases, until the values become about the same in Groups 4A and 4B.

13. The rare earths are put in the third group, since their valence is three, and since if they are distributed around the table there are not enough known and undiscovered elements together to go around. Cerium may be classified either with the third or the fourth group. A discussion

of this minor question is given. The elements of the rare earth group (not including yttrium or cerium) decrease in basic properties as the atomic weight increases, which is exactly the opposite of the general rule. As has been explained in the paper, in the rare earths the atomic number, and therefore the nuclear charge, keeps on increasing, while the valence remains constant. On the other hand, it seems probable that the atomic volume tends to keep on as it usually does, but this tendency is masked partly by another influence which tends to keep the atomic volume constant. The rare earths lie on the front of the table, where the elements in general become less basic as the atomic number increases, so they, in this case, as they probably do with atomic volumes, effect a compromise between this tendency and that which seeks to cause the elements in a single group to become more basic with increase in atomic weight. The resultant effect is that they become less basic as the atomic number increases, but not with anything like the rapidity which would be shown if they were to go around the table in the usual manner. In this sense the rare earth group forms a loop of its own, but a loop of practically constant valence.

14. The periodic table shows the relation between the properties of the elements and the nuclear charge, and this is presumably equal to the number of external electrons. It is probably the spacing and arrangement of these electrons which determines the chemical and most of the physical properties of the elements.

15. In Table II it may be seen that the spiral forms a series of lines which in any part of the table lie very nearly parallel. This is a graphical expression of the well-known fact that the atomic weights increase in a very regular way in any one group, and at about the same rate in all of the groups. This regularity may be explained on the basis of the theory of Harkins and Wilson, that the nuclei of the elements are built up from hydrogen and helium nuclei, according to a regular system, according to which the differences in mass in any one group are generally due wholly to differences in the number of helium nuclei present, at least in the case of the lighter elements.

16. In Fig. 4 and 5 the relations of the radioactive elements to the periodic table have been given. The nature of isotopes is discussed.

17. A number of figures and tables have been given to illustrate the relationship between the cohesive properties of the elements and the periodic system. The following properties have been plotted graphically: Melting points, with lines of maxima and primary and secondary minima, atomic volumes, density, cubic coefficients of expansion, compressibility, susceptibility, atomic frequency, elastic properties, cohesion and hardness. For the discussion of the relations between these properties the body of the paper should be consulted.

18. A theory as to the factors conditioning variations of cohesion is given.

19. The ordinary theory, that the atoms in solids do not occupy all of the space is supported.

Several problems related to the periodic system are now under investigation in this laboratory. One of these is the endeavor to prove whether or not the exceptional atomic weight of chlorine is due to its existence in two isotopic forms. This is a very important problem in its bearing on the theory of complex atoms, whatever may be the facts. Work is also being done upon the melting point of lead derived from radium. A third problem is the attempt to prove whether ordinary lead is or is not a mixture of isotopes.

The writers wish to thank Mr. W. A. Roberts for aid in the construction of the model of the periodic system.

The next paper in this series will be on "The Evolution of the Elements and the Stability of Complex Atoms."

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

THE DENSITY OF LEAD FROM RADIOACTIVE MINERALS.

BY THEODORE W. RICHARDS AND CHARLES WADSWORTH, 3RD.

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The startling differences observed by several investigators¹ in the atomic weight of lead from radioactive sources obviously suggest that other properties also may vary in different specimens; and the comparison of these may be of service in tracing the true causes of the differences in atomic weight. The phenomena are of interest whether or not one accepts the plausible hypothesis of Soddy and Fajans concerning the "isotopes." In a new field of this sort, of course, as great a variety of facts as possible is peculiarly important.

The present paper details one of a number of lines of research in this direction which are in progress in this laboratory, with the idea of finding out more about the substance admixed with ordinary lead in radioactive minerals—a substance so like ordinary lead that the usual modes of purification do not separate it, and that it produces no change in the ultra-violet spectrum.

The first among the properties to be studied was density.² The densi-

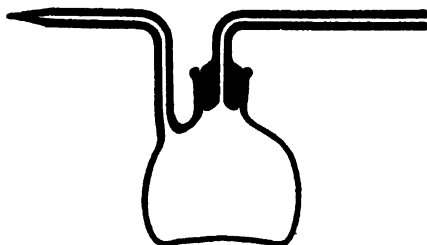
¹ Richards and Lember, *THIS JOURNAL*, 36, 819 (1914); Honigschmid and St. Horovitz, *Compt. rend.*, 158, 1798 (1914); M. Curie, *Compt. rend.*, 158, 1676 (1914); Soddy and Hyman, *J. Chem. Soc.*, 105, 1402 (1914); also especially, Hönigschmid, *Sitzb. k. Akad. Wiss. Wien.*, 123, IIa (Dec. 1914).

² The density of lead from thorianite has already been studied by Soddy, and discussed by Lindemann, respectively, *Nature*, 94, 615 and 95, 7 (1915). Professor F. W. Clarke has kindly called our attention to the desirability of studying also several other properties.

ties of the elements have assumed peculiar interest ever since Mendeléeff and Lothar Meyer, in 1869, showed this property to be a periodic function of the atomic weight. If the various isotopes have, as would be expected from the atomic volume curve, nearly if not quite the same atomic volume, then of course the isotope with less atomic weight should have less density. The matter was, therefore, inevitably approached with a preconceived opinion, but during the experimental work the investigators tried to make themselves as independent as possible of any preconceived notions. Preliminary experiments gave evidence that a difference in density really exists; hence the matter seemed worthy of the more careful experiments detailed below.

Apparatus.

Among the various forms of pycnometer available for determining the density, a form was chosen which for many years has been in use at Harvard, having been designed by one of us in 1898. No adequate description of this apparatus has ever been given, however, hence a brief



account of it is now in place. It consists in principle simply of an Ostwald-Sprengel pycnometer modified for use with solids by the introduction of a glass stopper, as indicated in the diagram, and has the ease of adjustment familiar to those who have used the Ostwald form. Several

details concerning it should be mentioned. In the first place, the stopper should not be too nearly cylindrical. In a stopper 8 mm. high the upper diameter should be 8 mm. and the lower 7. With this angle the stopper attains on successive settings almost precisely the same point, but is not so conical as to fall out easily. When the joint is very thoroughly ground, it is sufficiently watertight for long periods even without a lubricant, but certainty of closure is increased by spreading about 0.5 mg. of a lubricant (such as a mixture of hard and soft paraffin and melted rubber) upon the ground joint. This precaution was adopted in the present research.

For the best results, the pycnometer should of course be but little larger than the bulk of the substance to be studied; and the internal diameter of its tubes should not exceed 1 mm. Both of these specifications have been recently unheeded by a German firm which has advertised it.

To determine its volume the instrument was filled either with hot water, or else in an evacuated apparatus with cold previously boiled water. The two methods gave identical results. It was then left for a long time in an accurately adjusted thermostat kept at 19.94°.

Before weighing, the pycnometer was always wiped with a clean, lint-free cloth and was weighed in a balance case containing no drying agent.

Twenty minutes in the balance case sufficed amply for the attainment of constant weight, which did not change on standing twenty minutes more.

The following readings of the weight of water contained in the pycnometer—two settings and weighings for each of three adjustments of the stopper—show how accurately the instrument serves its purpose:

TABLE I.—WEIGHTS OF WATER REDUCED TO VACUUM STANDARD.
TEMPERATURE 19.94°.

5.7264	5.7264	5.7264
5.7264	5.7263	5.7264.

Five of these six weighings were identical and the other differed only by 0.1 mg.

The pycnometer was used with the lead in the same way as with water alone. After drying in an air-bath a thin coating of the lubricant was smeared upon the ground glass stopper. A carefully weighed quantity of lead, prepared in a manner to be described later, was introduced after weighing the pycnometer with its lubricant; and in the first series of experiments (called "1st method" in the table below) the vessel was filled through the pointed jet with pure hot water, which, if previously boiled, was found to be without action on the lead. The pycnometer was then placed in the water of a clean thermostat carefully regulated to within one-hundredth of a degree and allowed to come to thermal equilibrium. After the setting of the meniscus, the pycnometer was removed, and carefully dried and reweighed—just as it had been when containing water alone. In the experiments designated "2nd method" in the table below, the filling was conducted with cold boiled water in a vacuum according to the method used by Kahlbaum and others.¹ This is by far the more trustworthy method with a porous substance, but it will be seen that in the present simple case the two methods gave essentially identical results.

Preparation of Materials.

The best method of purifying lead salts is by crystallization of the nitrate.² A large quantity of lead from radioactive sources (obtained through the kindness of Mr. S. Radcliff and Mr. E. R. Bubb, of the Radium Hill Co. of Australia) was dissolved in nitric acid and the nitrate was recrystallized five times by dissolving the crystals in hot water and adding a large excess of nitric acid. In this way the crystals separated from a large volume of mother liquor and the purification was very rapid. The pure nitrate was then divided into several portions, of which one was immediately afterward electrolyzed in quartz vessels from hot solution, using electrodes of platinum wire. This procedure gives a very beautiful crystalline deposit, which is easier to wash and for this reason purer than

¹ *Z. anorg. Chem.*, 29, 237 (1901).

² Baxter and Grover, *THIS JOURNAL*, 37, 5 (1915).

the somewhat spongy deposits obtained from cold solution. The subsequent treatment of these crystals will be described later. (Sample C.)

Another portion of the pure lead nitrate was precipitated as chloride by pure hot hydrochloric acid obtained by distilling pure acid of constant boiling point. The precipitate was thoroughly washed and recrystallized as chloride four times. This chloride was then electrolyzed, using a fine-grained porous cup to surround the anode, in hot, slightly acid solution; and the crystals of lead thus obtained were thoroughly washed and treated like the preceding. (Sample D.)

Finally, samples of ordinary lead chloride, which had been carefully purified by Dr. J. W. Shipley, were treated in the same way. This lead chloride had been twice recrystallized after precipitation from a solution of the acetate which had itself been several times recrystallized. The electrolytic crystals of pure ordinary lead were thoroughly washed and treated like the radioactive metal. Two such preparations were made and designated A and B.

Each of these samples of clean lead crystals was finally fused in a mould of pure sugar charcoal made for the purpose. This mould or boat had been made from a paste of powdered sugar charcoal, sugar and water, packed into an "alundum" boat, moulded into the desired shape, heated cautiously in an air bath, and when dry thoroughly ignited before the lead was placed upon it. Upon the hard, smooth surface of this charcoal boat each bar of lead was melted, the boat having been placed in a hard glass tube, in a current of pure, dry hydrogen. This, in turn, was made from the electrolysis of sodium hydroxide containing some baryta, passed over red hot copper, and finally dried by potassium hydroxide previously fused with a little permanganate. The resulting bars of lead were beautifully bright and clean. After cooling, each was removed, carefully freed from adhering carbon, cut into small pieces and hammered on a polished anvil with a clean steel hammer. Finally these hammered bars were scrubbed with clean sea-sand, dried and polished with a clean cloth and placed in a desiccator over fused potash. Each of the three samples was subjected to precisely the same treatment, so that no difference in density could arise from any difference in the preparation of the metal.

With each of these varieties at least four determinations of the density were made, using different amounts of material, so as to be sure that no systematic error existed in the method. The data are given below in full, the weighings both in air and corrected to vacuum being recorded. It will be remembered that the weight of water contained by this pycnometer was 5.7264 g. in vacuum; the average amount in air being 5.7203. The temperature was in every case 19.94°.

TABLE II.—DENSITY OF COMMON LEAD. TEMPERATURE 19.94°.

Method.	Sample.	Obs. weight of lead.	Weight of lead in vac. (W).	Obs. wt. water not displaced.	Corresp. volume.	Volume of Pyc.	Volume V of water (displaced).	Density W/V.
1st	A.....	11.3274	11.3270	4.7236	4.7369	5.7364	0.9995	11.333
	A.....	5.7889	5.7887	5.2111	5.2258	5.7364	0.5106	11.337
	A.....	5.5202	5.5200	5.2348	5.2496	5.7364	0.4868	11.339
2nd	A.....	7.3297	7.3294	5.0758	5.0901	5.7364	0.6463	11.341
	B.....	15.9150	15.9144	4.3205	4.3327	5.7364	1.4037	11.337

Av., 11.337

TABLE III.—DENSITY OF RADIOACTIVE LEAD. TEMPERATURE 19.94°.

Purified by 5 recrystallizations of nitrate.

1st	C.....	13.5713	13.5708	4.5217	4.5345	5.7364	1.2019	11.291
	C.....	8.2967	8.2964	4.9874	5.0014	5.7364	0.7350	11.288
2nd	C.....	13.4788	13.4783	4.5294	4.5422	5.7364	1.1943	11.286
	C.....	7.5013	7.5010	5.0576	5.0719	5.7364	0.6645	11.288

Av., 11.288

Further purified by 5 recrystallizations as chloride.

1st	D.....	12.9527	12.9522	4.5764	4.5893	5.7364	1.1471	11.291
	D.....	7.9345	7.9342	5.0196	5.0338	5.7364	0.7026	11.292
2nd	D.....	11.5183	11.5179	4.7026	4.7159	5.7364	1.0205	11.287
	D.....	6.6672	6.6670	5.1312	5.1457	5.7364	0.5907	11.287

Av., 11.289

Hence the results are as follows:

Density of ordinary lead.....	11.337
Density of radioactive lead from nitrate.....	11.288
Density of radioactive lead from chloride.....	11.289

Evidently the density of the lead from radioactive sources is 0.049 that is to say, 0.43% lower than that of ordinary lead—a very striking difference, in the sense which was expected.

Before considering these results further, the results of others on the density of ordinary lead may receive a moment's consideration. As usual, these are highly conflicting, for the determination of the density of solids has been highly uncertain; good results are rare. Earlier values for the density of lead have varied from 11.19 to 11.37.¹ The most accurate of these seems to have been that of Kahlbaum, Roth and Siedler, who, however, used only distillation as a means of purifying their metal. Their values were 11.341 and 11.347 for unpressed and pressed lead, respectively.² As they themselves showed that the common metallic impurities in lead were easily volatile under the conditions which they employed, and, therefore, might have contaminated their distillate, their result, although good, cannot be deemed certainly accurate. The qualitative experiment in

¹ See, for example, Kahlbaum and others; *Z. anorg. Chem.*, 29, 278 (1901).

² *Z. anorg. Chem.*, 29, 280 (1901).

which they distilled a ten-pfennig piece is hardly convincing as evidence of precision.¹ Of course these criticisms do not apply to their interesting conclusions about the effect of pressure, except insofar as possible impurities might affect the crystalline habit of the solid metal, and perhaps cause small vacant spaces in the structure.

The difference between the result of Kahlbaum and his collaborators, 11.341, and our result, 11.337, for ordinary lead, is only 0.004 or 0.04%. As density determinations go, this is a good agreement. The only impurities likely to have been in our sample are hydrogen and carbon, which might possibly cause a deviation of this magnitude, although we have no definite evidence that either of these elements is soluble in melted lead to an appreciable extent. Another possible cause of difference lies in a conceivable allotropy in the metal.²

Whatever may be the cause of this slight difference, it does not affect the arguments to be drawn from our comparative results, for each of our samples of metal was treated precisely in the same way. Hence each sample of lead must have been equally saturated with carbon and hydrogen, if any dissolved, and each must have been of the same modification. It will be noted that the greatest deviation from the mean is 0.004 in the case of the common lead and only 0.003 in the case of each sample of radioactive lead. The difference, on the other hand, between ordinary lead and the mean of the two samples of radioactive lead is, as has been said, 0.049, over twelve times the greatest deviation from the mean and over twelve times the difference between our pure lead and that of Kahlbaum and his collaborators. There can be no question, therefore, that these results show a real difference between the two kinds of lead, which must be referred to the admixture causing the low atomic weight of radioactive lead.

Furthermore, it should be noted that the five additional recrystallizations of the second radioactive sample (D) as chloride produced no essential change in the purity of the lead, as indicated by its density. Hence it is clear that more drastic means than recrystallization must be taken to separate the modifications.

It is interesting to compare these results with those of Soddy, who found in lead from thorite slightly higher density than that of ordinary lead³—just the opposite to the phenomenon described in this paper. Soddy earlier found in lead from thorite (presumably a similar sample) also an atomic weight higher than that of ordinary lead, whereas the atomic weight of our Australian radioactive lead has been found, in experiments not yet published, to be much lower than that of ordinary lead, namely 206.3 instead of 207.2. Hence Soddy's results are not inconsistent

¹ *Loc. cit.*, p. 195.

² Cohen and Inouye, *Chem. Weekblad*, 1910, p. 1.

³ *Loc. cit.*

with ours. They seem rather to indicate that a different admixture was present in his material.

Returning to our results, it is interesting to note that the atomic volume of the Australian radioactive lead is very nearly the same as that of ordinary lead, because $206.3/11.288 = 18.276$, whereas for ordinary lead $207.2/11.337 = 18.277$. The difference between these values for the atomic volume is so small as to be no greater than the probable limit of error of the experiment. Hence it is clear that the atomic volume of radioactive lead is essentially equal to that of ordinary lead.

Of course, no one knows as yet what proportion of impurity exists in this radioactive sample, which doubtless contains some ordinary lead. If the true atomic weight of the pure isotope is really 206, this sample must have consisted chiefly of the isotope, and the atomic volume of the pure isotope must be very nearly 18.3. On the other hand, it is possible that the theory is incomplete and that the lowering of atomic weight and density is due to the admixture of a much smaller amount of a substance with much lower atomic weight. In that case the atomic volume of the admixture is, of course, less certain, but it probably is near 18.

It is a pleasure to express our indebtedness to the Carnegie Institution of Washington for generous pecuniary support in this investigation.

Summary.

The density of ordinary lead (having an atomic weight of 207.2) and of lead from Australian radioactive sources (having an atomic weight of 206.3) was carefully determined in a convenient pycnometer which is described in detail for the first time, although long in use. The density of ordinary lead reduced to the vacuum standard was found to be 11.337, and that of radioactive lead 11.288. Continued fractionation produced no change in this low density, and it could not have been due to any irregularity in preparing the metal since the samples were all prepared in the same way. This difference in density is especially interesting, because it almost exactly parallels the difference in atomic weight. Thus the atomic volume of radioactive lead is found to be almost exactly equal to that of ordinary lead, the figures being each very nearly 18.28.

CAMBRIDGE, MASS.

A THEORY OF CHEMICAL REACTION AND REACTIVITY. FURTHER NOTE.¹

By E. C. C. BALY.

Received December 26, 1915.

In the addenda to his original criticism, Dr. Dehn has carried the matter no further. I will therefore only add very few words.

¹ This reply was received too late to be published in the January number of *THIS JOURNAL*, as was originally intended.—EDITOR.

In the first place, Dr. Dehn makes a statement that is absolutely untrue and to which I give unhesitating and categorical denial. He says that I devote more than half of my reply to "discussing new physical data not published by him (Baly) when his theory appeared in *THIS JOURNAL*." These data were published in the *Philosophical Magazine* many months before the paper under discussion.¹ Dr. Dehn's accusation is all the more strange in view of the fact that he includes these two papers in his list of my publications.

In the second place, referring to the changes in absorption with concentration, Dr. Dehn makes the surprising statement that "we must assume not only an infinite series of absorption curves but an infinite series of reactivities. * * * * * These results of course are contrary to fact as *acknowledged by Baly in his reply*." I pointed out in my first reply that Dr. Dehn had got very mixed in his ideas as regards the effect of concentration and by the misuse of the word "band" where "band group" is meant. I said that his criticism therefore falls to the ground and that his statement is absurd. The only notice he takes of this is to add the words which I have italicized above. I am accused of a great sense of humor by Dr. Dehn, but I am sadly afraid that it is not as great as his.

In the third place, the new paragraph added by Dr. Dehn beginning "There can be no quibble that Baly believes, etc.," and indeed also the succeeding paragraphs reveal such a serious number of misconceptions and misconstructions, which I can no longer believe to be without prejudice, that further discussion has become valueless.

THE UNIVERSITY, LIVERPOOL.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE DROP WEIGHT METHOD FOR THE DETERMINATION OF SURFACE TENSION.²

(SURFACE TENSION I.)

BY WILLIAM D. HARKINS AND E. C. HUMPHERY.³

Received October 22, 1915.

The two methods in most general use for the determination of the capillary constants of liquids are the capillary tube and the drop weight methods. Of these two, the first is much the more sensitive to the action of impurities, since the surface of the liquid involved in the measurement is made very small, while in the drop weight method the surface is not

¹ *Phil. Mag.*, 27, 632 (1914), and 29, 223 (1915).

² Read before the National Academy of Sciences, December 7, 1914.

³ This series of papers on surface tension has been presented to the University of Chicago by E. C. Humphery as a dissertation in part fulfillment of the requirements for the degree of Doctor of Philosophy.

only made relatively large but it is also renewed much more easily. It is not surprising, therefore, that the most concordant results on the surface tension of a single liquid are obtained by the drop weight method, and that duplicates run by this method, when it is properly applied, show a most remarkable agreement. However, when the results obtained by different workers on different liquids by this method are compared with determinations made by other methods, it is found that they show just as remarkable a disagreement, the deviation in some cases rising to 20%, or even 40%. These very bad results are due however, not to any inherent fault in the method, but to the application of a very faulty theory. Thus many workers have used the equation

$$W = 2\pi r\alpha, \quad (1)$$

where W is the weight of the drop, r the radius of the tip of the dropping tube, and α the surface tension. This equation would be true only when the pendant drop is supported entirely by the surface tension of the surface film at the edge of the tip, and when all of the pendant drop falls, but this is very far from the truth, for the drop which falls is nowhere nearly all of the pendant drop.

The most complete treatment of the mathematical theory of the relation between the forms of drops and surface tension is given in a book published in 1883 by Bashforth and Adams.¹ Much later than this, in 1906, Lohnstein² applied the general theory to the special case of the hanging drop just before its fall, and the residue left after the fall, and from the difference he obtained the magnitude of the falling drop itself. By doing this he was able to reduce the problem, which would otherwise be of a kinetic form, to the solution of problems in statics. In solving the problem it was necessary for Lohnstein to make an assumption in regard to a relationship between the form of the drop just before it falls, and that of the residual drop left immediately after the fall. The cross sections of the drop as it increases in size give a family of curves which have different values of a variable parameter. Two values of this parameter give two curves which have the same tangent at the point of contact with the tip. Lohnstein assumed that the drop which remained after the fall had a cross section which gave a curve with the same angle of contact with the tip as the drop just before it fell. In calculating the size of the falling drop, then, he subtracted the volume of the drop with the parameter p from the volume of the drop with the parameter p' , where the two curves, due to these different parameters, have the same tangent at the point in which the drop meets the tip. The curve with the parameter p' gives the form of the drop before the fall, and the curve with the parameter p gives the form of the drop remaining after the fall.

¹ "Capillary Action," Cambridge University Press (1883).

² *Ann. Physik*, [4] 20, 237-68, 606-18 (1906); *Z. physik. Chem.*, 64, 686 (1908); 84, 410 (1913.)

The equation obtained by Lohnstein for the weight of the falling drop is

$$W = 2\pi r \alpha f(r/a), \quad (2)$$

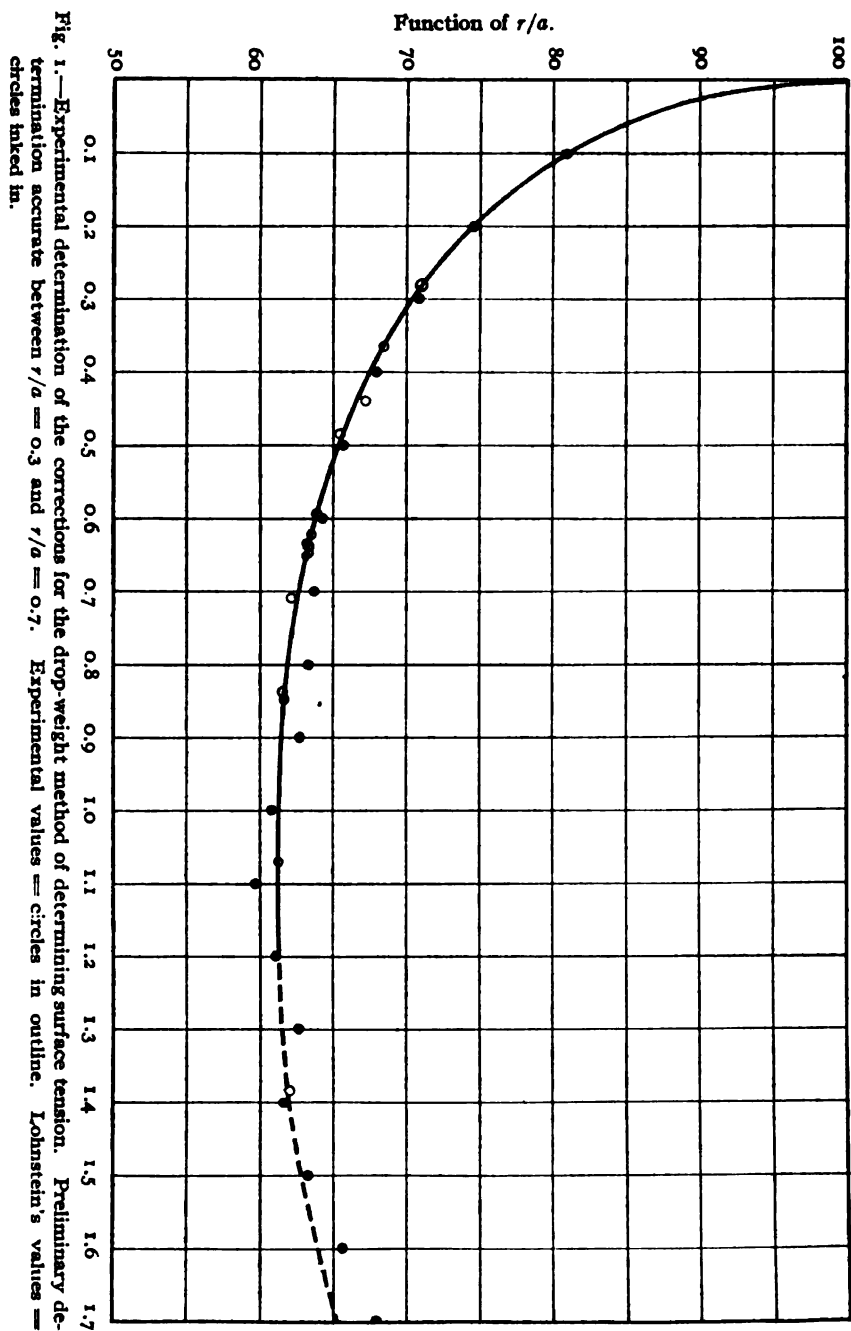
where r is the radius of the tip and a is the square root of the capillary constant, and $f(r/a)$ represents a function of r/a . The surface tension is given by the equation

$$\alpha = W/2\pi r f(r/a), \quad (3)$$

and since $f(r/a)$ varies from 1.0 to 0.6, it is evident that results obtained by the older equation (1) may be increased by as much as 65% by the application of this correction. Lohnstein determined the values of the function of r/a for different values of r/a , and his calculation of these corrections from a theoretical standpoint makes it possible to use the drop weight method for the determination of surface tension, and, since, as has been stated, this is the most exact from an experimental standpoint of the methods used in work on capillarity, Lohnstein's work represents a great advance in our knowledge of this fundamental subject.

Unfortunately, however, when it becomes desirable to determine the surface tension by this method, it is found that Lohnstein did not carry his calculations of these corrections to a sufficient degree of accuracy to make this method available for determinations where an accuracy greater than 4% is desired. It is therefore important that this correction, which is a very fundamental one in work on capillarity, should be determined with a greater degree of accuracy. For this purpose the apparatus devised by the writers¹ seemed to make it possible to make determinations of this correction under conditions which are more nearly ideal than is possible by the ordinary methods. Thus the substitution of work on the liquid-liquid interface for the ordinary method in which a liquid-air interface is used makes it possible to compare the drop weight results with those obtained in a capillary tube of large bore (1.4 mm.) when the capillary rise is great enough (78.0 mm.) to give accurate measurements. Not only can the diameter of the large capillary be determined more accurately than that of the smaller tube used for measurements on a single liquid, but in addition it is much easier in the large tube to keep the surface of the meniscus in a pure condition. Then in the drop weight determination itself, the drop falls very much more slowly when it falls into a liquid than when it falls into a gas, so that there is less disturbance in the drop at the time of fall than when it breaks away at a relatively high speed. The corrections determined in this way are given in Table I, and are shown in the form of a curve in Fig. 1. In the figure the ordinates represent the values of the function of r/a , and the abscissae give the values of r/a . The circles which are inked in represent Lohnstein's theoretically determined values, while the circles given in outline give the new

¹ Described in the paper which follows.



values determined experimentally. The figure shows that the experimental values give with Lohnstein's first two points for small values of r/a , a much smoother curve than is given by his own theoretical values. The experimental values were determined by the use of a number of different liquids, and measurements were made both upon liquid interfaces, and at the surface of a single liquid. Table II gives a list of the corrections for round values of r/a .

TABLE I.—EXPERIMENTAL CORRECTION FOR DROP WEIGHTS.

Point No.	r/a .	$f(r/a)$.	Interface.	Temperature.
1	0.281	0.709	Water—Ethyl carbonate	(25°)
2	0.366	0.685	Water—Benzene S. T.	(25°)
3	0.441	0.672	Water—Dimethylaniline	(25°)
4	0.484	0.654	Water—EtCO ₂	(25°)
5	0.592	0.639	Water—Benzene	(10°)
6	0.621	0.636	Water—Benzene	(20°)
7	0.633	0.632	Water—Xylene	(25°)
8	0.636	0.634	Water—Benzene	(25°)
9	0.648	0.634	Water—Benzene	(30°)
10	0.649	0.632	Water—Toluene	(25°)
11	0.709	0.620	Water—Air	(25°)
12	0.837	0.615	Water—Hexane	(25°)
13	0.845	0.616	NaCl Soln.—Benzene	(25°)
14	1.071	0.612	Benzene—Air	(25°)
15	1.387	0.620	SrBr ₂ Soln.—Hexane	(25°)

TABLE II.—CORRECTIONS FOR DROP WEIGHT—FROM CURVE.

r/a .	$f(r/a)$.	r/a .	$f(r/a)$.
0.0	1.000
0.1	0.805	0.9	0.614
0.2	0.741	1.0	0.612
0.3	0.703	1.1	0.612
0.4	0.676	1.2	0.613
0.5	0.655	1.3	0.615
0.6	0.637	1.4	0.620
0.7	0.625	1.5	0.629
0.8	0.618 See note (1)	1.6	0.641

The correspondence between the experimental results and the smooth curve drawn through Lohnstein's first two points, and the additional fact that the experimental curve follows the general trend of Lohnstein's values, shows that the relationship thus developed theoretically by Lohnstein must be, on the whole, the correct one. However, some prominent

¹ For values of r/a greater than 0.7 the values are only approximate, since enough determinations have not been made in this region to fix these values with certainty. The indications are that if any change is shown by further experiments the change will be such as to *decrease* the values here given. They already represent a considerable *decrease* in comparison with the results obtained by Morgan, when he uses the work of Ramsay and Shields and other investigators in order to obtain the constant in this equation.

workers on surface tension still refuse to accept the validity of Lohnstein's work and prefer to use in place of his relationship the so-called law of Tate. The law of Tate states that the weight of a drop falling from a tube is proportional to the radius of the tube and to the surface tension of the liquid. Thus Morgan, in a paper printed in 1915 and entitled "Das Tatesche Gesetz, Eine Antwort an Herrn Lohnstein," states as the conclusion of one of his sentences

"Man muss folgern, dass die form des Tateschen Gesetzes $\gamma = K\omega$ für die benutzten Mundstücke ein wahres und strenges Gesetz ist."

If Tate's law holds the ratio $\frac{\text{Drop weight}}{\text{Tip diameter}} = K$.

Morgan gives the results of work upon 16 tips varying in diameter from 3.05 to 7.86 mm. in confirmation of this law. In order to see the relation of this work to the experimental correction curve, the corrections have been calculated from Morgan's values (Table III) and plotted in

TABLE III.—CALCULATION OF $f(r/a)$ FROM MORGAN'S RESULTS.

Benzene.		Quinoline.		Pyridine.		Carbon tetrachloride.		Ether.	
S. T. = 26.92.		S. T. = 42.66.		S. T. = 35.33.		S. T. = 24.89.		S. T. = 15.33.	
$t = 27.8$.		$d = 1.08755$.		$d = 0.97365$.		$d = 1.57528$.		$d = 0.7045$.	
$a = 2.5117$.		$a = 2.829$.		$a = 2.708$.		$a = 1.795$.		$a = 2.107$.	
r/a .	$f(r/a)$.	r/a .	$f(r/a)$.	r/a .	$f(r/a)$.	r/a .	$f(r/a)$.	r/a .	$f(r/a)$.
0.607	0.6595	0.539	0.673	0.5605	0.6573	0.8494	0.6377	0.7238	0.6569
0.782	0.636	0.6946	0.6434	0.7222	0.6425	1.095	0.6273	0.9326	0.636
0.796	0.6356	0.707	0.643	0.7355	0.636	1.114	0.6268	0.9749	0.6359
0.8978	0.6237	0.797	0.624	0.8288	0.623	1.256	0.6237	1.070	0.6234
0.9356	0.6226	0.880	0.624	0.915	0.623	1.309	0.6275	1.182	0.623
0.9913	0.6227	0.972	0.624	1.011	0.6225	1.387	0.631	1.305	0.6227
1.057	0.6227	1.006	0.624	1.022	0.622	1.479	0.6376	1.350	0.626
1.095	0.6223	1.034	0.6213	1.075	0.622	1.532	0.643	1.388	0.6264
1.133	0.622	1.096	0.6215	1.204	0.622	1.585	0.651	1.554	0.642
1.165	0.621	1.158	0.622	1.257	0.6224	1.639	0.658	1.623	0.647
1.234	0.6223	1.209	0.6214	1.352	0.6257	1.727	0.660	1.754	0.6613
1.304	0.6256	1.306	0.6248	1.444	0.630	1.824	0.6636	1.865	0.6757
1.362	0.6297	1.392	0.6294	1.905	0.671
1.471	0.639
1.565	0.6465

Fig. 2. Morgan has not, in any of these cases, determined the absolute surface tension himself, since his work gives only relative values, so the vertical position of his curves as a whole is dependent upon the value which he chooses as the surface tension of his standard liquid. Now the values of these surface tensions are taken from the work of others, and are usually the result of work by the capillary tube method. It is therefore evident that the curves representing Morgan's work as given in Fig. 2 may be brought down to the same general level as the experimental

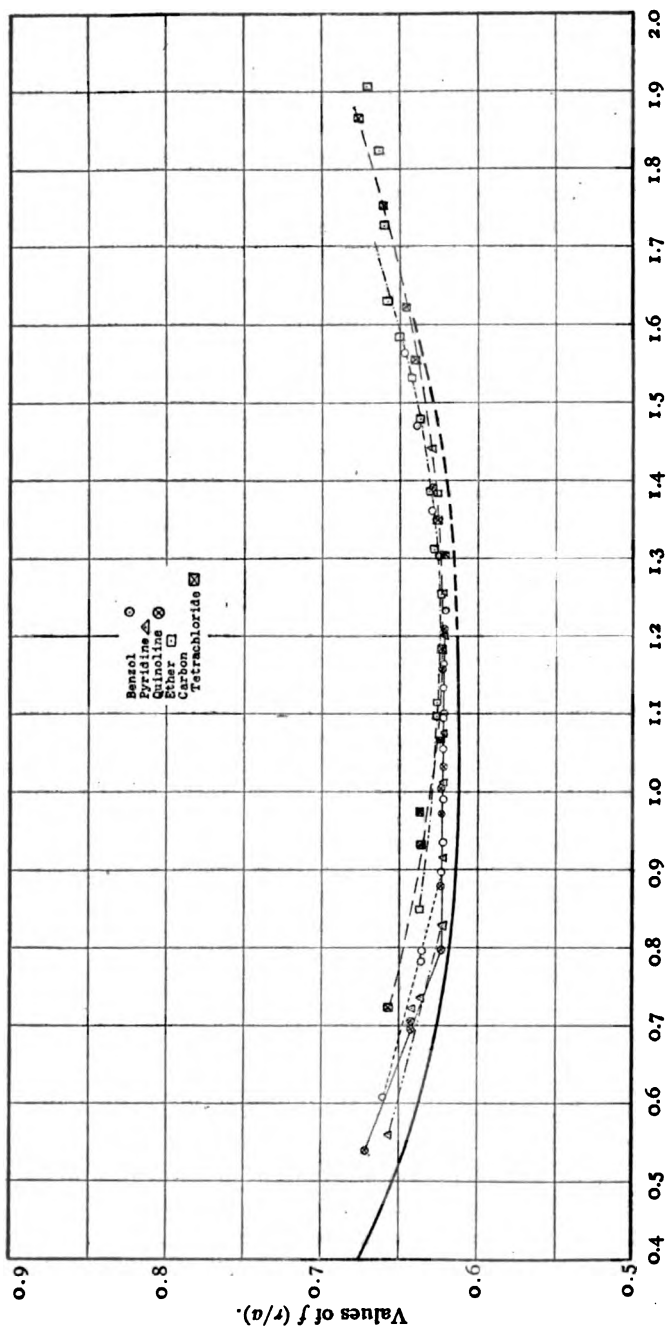


Fig. 2.—Values of the drop-weight correction calculated from Morgan's work with the theoretical curve given below for comparison.

correction curve, but the curves cannot be made coincident. The law of Tate might be said to hold over the region where the correction curve is horizontal, but this is the case only where the curve and its horizontal tangent become the same. This is not strictly the case for any part of the correction curve, but when the corrections are determined from Morgan's work it is seen that a large number of the points do lie on a straight horizontal line; on the other hand a large number of points lie very far from this straight line. In comparing the two results it should be remembered that the lower the correction factor, and therefore the lower the curve, the higher the surface tension, so that values obtained from the correction curve determined by the writers would be higher than those corresponding to Morgan's values.¹

Such great care has been taken by Morgan in his work that it would seem worth while to endeavor to find a cause for the fact that the correction curve determined by us is so closely in accord with Lohmstein's theoretical work, and that the values given by Morgan for small values of r/a deviate so widely from the general form of the correction curve. This work is now being done by Mr. E. D. Wilson in this laboratory. He is beginning the work with the aim of making more complete calculations than those of Lohmstein, and at the same time to introduce into the equations such factors as viscosity, in order to see what would be the result of variations in these properties. The deviations in Morgan's work do not follow the order which would be given them by a variation of any one of the following properties of the liquids: viscosity, vapor pressure, density; but it is of course possible that more than one of these may be effective at the same time. The effect of differences of vapor pressure in changing the volatility of the liquid should not enter into the equations, since such effects should be eliminated by the experimental methods.

The use of very small tips makes the value of the function of r/a approach the value one, but the slope of the curve for these very small values of r/a is so great that it is difficult to tell exactly what correction to apply. This is illustrated by the irregularity in the corrected results of Antonow

¹ That our *lower* values for the correction factor, that is, the *higher* values for surface tension are more apt to be the better, is confirmed by the recent work of Richards and Coombs, *THIS JOURNAL*, July, 1915, who obtain surface-tension values for benzene which are considerably higher than those found by the capillary-tube method by Ramsay and Shields, Renard and Guye, and Walden and Swinne. The deviation is of the order of 3%. The fact that Morgan's results give a higher correction factor than ours does not mean, therefore, that his drop weights are as a whole too low, but it indicates that the capillary-height method has in the past given results which are in general too low, for Morgan has not used any capillary-height measurements of his own, but seems to have determined the constant of his equation from the average capillary height determinations of other investigators. The discrepancy is therefore due, in all probability, to errors in the capillary-height methods and, not to deviations in the weights of the drops themselves.

on the surface tension at the interface water-benzene, as given in Table IV, where the variation amounts to 8% of the maximum value.

TABLE IV.—ANTONOW'S DETERMINATIONS OF THE SURFACE TENSION AT THE BENZENE-WATER INTERFACE BY THE USE OF EXTREMELY SMALL TIPS.

Radius in mm.....	0.13	0.175	0.350	0.630
α_{18}° corrected.....	34.93	36.04	37.97	35.40

The value obtained by the writers with larger tips is 34.18 dynes.

The correction curve is now most accurately known between the values of r/a from 0.3 to 0.8, since that is the more common range for the tips which have been available for work on the liquid-liquid interface. Seven new tips are now available for use and the corrections from 0.8 to larger values of r/a will be made more accurate by further work.

The writers wish to express their indebtedness to the American Academy of Sciences, Arts, and Letters for a grant of three hundred dollars from the C. M. Warren Fund. The grant will be used in a continuation of this research. The work described in papers II, III, and IV of this series has been accomplished by the use of this fund.

CHICAGO, ILL.

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

APPARATUS FOR THE DETERMINATION OF THE SURFACE TENSION AT THE INTERFACE BETWEEN TWO LIQUIDS.

(SURFACE TENSION II.)

By WILLIAM D. HARKINS AND E. C. HUMPHERY.

Received October 22, 1915.

The surface tension at the interface between two liquids has been determined by a number of different methods,¹ but of these only two, the method of the falling drop, and the capillary-tube method, seem well adapted for general use. The importance of the interfacial tension in work in colloidal chemistry and in biological research, makes it essential that the apparatus for the determination of the surface tension should be of better design than that which has been used in most of the research work on this subject.

The Drop-Weight Apparatus.

The most essential features of a drop-weight apparatus are that the tip shall be ground almost perfectly round, with very sharp edges, and that the diameter of the tip shall be of the proper magnitude to give a ratio between the radius of the tip (r) and (a) the square root of the capillary constant, such that the Lohmstein correction² for the particular value

¹ For a critical account of twenty methods see "A critical paper by Ferguson," *Science Progress*, Jan., 1915, p. 428.

² For an explanation of the Lohmstein correction see the paper which precedes this one.

of r/a may be one which has been accurately determined, and also such that this correction shall not vary rapidly with the radius. The neglect of these essential conditions has been so general that this method in practically all of the previous work on interfacial tension has been very inaccurate. Thus Antonow in his fundamental work on the relation between the tension at the interface and that of the separate phases, evidently in the endeavor to make the correction factor close to unity, chose tips with very small diameters. This does, as a matter of fact, make the factor much closer to unity than if larger tips were to be used, but it also makes the correction vary greatly as the value of r/a changes. Thus the correction factor changes its value from 1.000 for $r/a = \infty$ to 0.741 for $r/a = 0.2$, or a variation of 25.9% over a range of 0.2. On the other hand, when larger tips are taken a variation of r/a from 0.9 to 1.2 changes the correction by only 0.2% as a maximum for a change of 0.3 in the values of r/a . For dropping water into other liquids the tip which has been used most largely has a diameter of 9.5 mm., which is very satisfactory, though when dropping water downward into other liquids, the diameter should be somewhat greater if it is desired that the correction factor shall be as constant as possible for different liquids. This is, however, not necessary, since the correction curve has a slight slope and is well determined in the range where this tip is used.

The apparatus, but not its supporting stand, is shown in Fig. 3. It consists of a pipet of a capacity of 10 cc. which for convenience should be made smaller if much smaller drops are to be obtained, either on account of the use of a smaller tip, or because of a greater difference of density between the two liquids. Above and below the bulb of the pipet the stem is graduated to 0.1 cc. so that readings may be made to 0.01 cc. In order to give a better control of the drop the long vertical capillary tube at the right is made as small as a diameter of 0.3 mm.

The short arm H at the right which has the tip at its lower end is sealed into a large glass stopper, E. The glass beaker F, which is used to hold the lighter liquid, is fastened to the glass stopper by means of a ground joint which is made with a very slight slope, and a longer line of contact than is shown in the figure. The apparatus is supported by a thick sheet of aluminium used as a back, and on the top of this rests a platform which supports a level. The level is set on adjusting screws, so that the end of the tip may be set horizontal. The back and the platform are supported by heavy horizontal rods which are clamped to a vertical 30 mm. rod. This is fitted into a heavy tripod with three leveling screws.

The lighter of the two liquids used in the determination is not usually put directly into the beaker F but into a smaller glass cylinder which rests on the bottom of the beaker, since the beaker is so large that it re-

quires a large amount of liquid. The apparatus is supported in a thermostat with the water level at L. The tube G is used to connect the beaker with the apparatus used for the production of a sufficient decrease of pressure so that the drop may be drawn over. This apparatus, while extremely simple, should be such as to give perfect control of the drop. It consists of a buret with two connecting tubes sealed on at the top. Each of these connecting tubes is fitted with a glass stopcock.¹

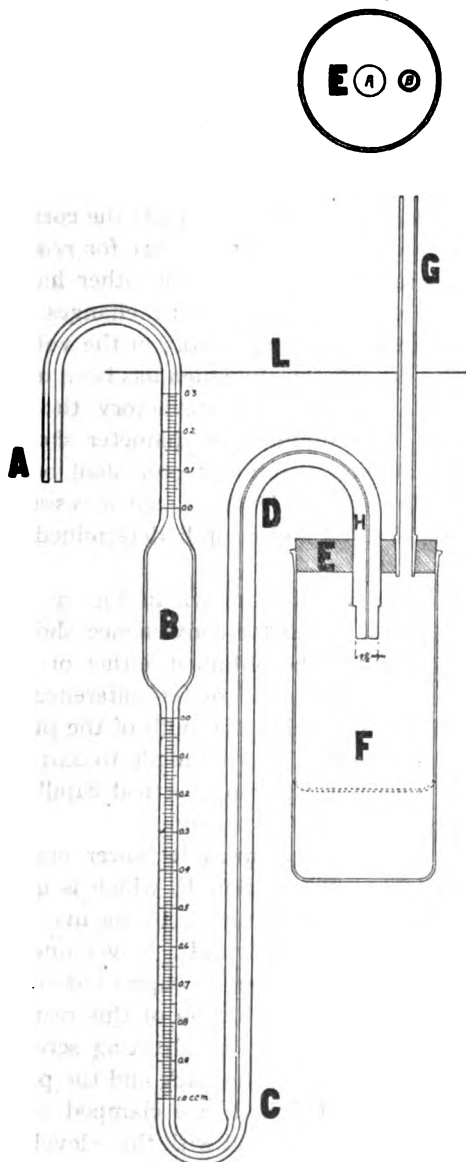


Fig. 3.—Glass parts of drop weight apparatus, for determinations at a liquid-liquid interface.

¹ For a description of this apparatus see paper by Harkins and Brown, p. 250.

The procedure used in making the determination is to first fill the pipet by suction until the liquid rises to the 0.2 or 0.3 mark on the upper graduation, the liquid is then allowed to run out until it stands at about the 0.0 cc. mark, when a clamp on the rubber tube fastened on the glass tube at A, is closed.

Then the cylinder containing the lighter liquid is adjusted in the beaker F and the metal shelf on which the beaker rests is lifted to hold it. Care should be taken that a sufficient amount of the liquid is used to raise its level about 1 cm. above the lower edge of the tip when the beaker is placed in its final position.

The apparatus is then lowered into the thermostat, and allowed to stand from 35 to 50 minutes before beginning the run. When the liquids have come to constant temperature the clamp at A is opened and the heavier liquid sucked back into the pipet until its surface is just beginning to enter the mouth of

the tip. The height of the liquid in the upper graduated tube is read off. The tube G is then connected by a rubber tube with the suction apparatus, which is filled with mercury, and enough mercury is at once run out so that the drop will fall in from 3 to $3\frac{1}{2}$ minutes. This causes the drop to form rapidly at first, and with extreme slowness just before the drop falls. If it is seen toward the end of the formation of the drop that the suction is insufficient to cause it to fall, the stopcock at the bottom of the suction buret is rotated quickly, thus allowing a very small amount of mercury to escape. The tube at the bottom of this buret is drawn down to a capillary in order to help keep this amount of mercury small. These precautions are taken so that the liquid in the drop, just before its fall, may be as free from currents, and from motion as a whole, as is possible. It is, of course, impossible to reduce the actual dropping of the drop to a static phenomenon.

As soon as the liquid in the pipet falls until its upper surface stands in the lower graduated tube, it is drawn back until it again just begins to enter the mouth of the tip, and the final reading of volume is taken under the same conditions as at the beginning of the determination.

In order that the volume of the drop may be converted into its weight in the lighter liquid, the densities of both liquids must be determined with a degree of accuracy which should be increased as the two approach each other in density. For the more accurate determinations a new form of pycnometer was devised, and this will be described in a later paper. **Apparatus for the Determination of the Surface-Tension at the Interface between Two Liquids by the Capillary-Tube Method.**

The apparatus used for the determination of the surface tension at the interface between two liquids by the capillary-tube method, is shown

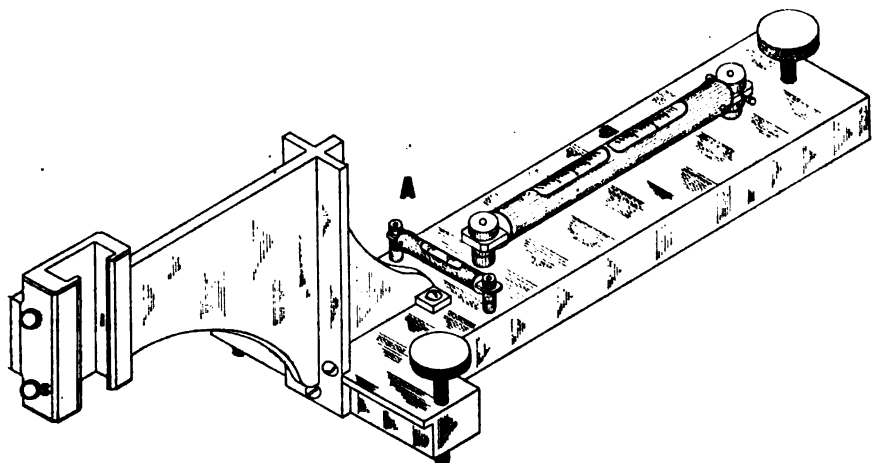


Fig. 4A.

in Fig. 4A, B, and C. The base of the stand A is filled with lead so that it may rest upon a supporting pillar and still support the capillary tube in the thermostat. The stand is provided with levels which are adjusted so that when they are level the capillary tube is vertical. The capillary tube is made from Jena capillary tubing and fits through the holes D, D. Its top rests against the stop E. The top of the tube serves only as a support for the lower part and may therefore be replaced by a metal tube or rod. The support B is first fastened in its supporting stand at I, and is fastened by the set screws S, S, against I, which is ground so that both surfaces which come together at I are flat.

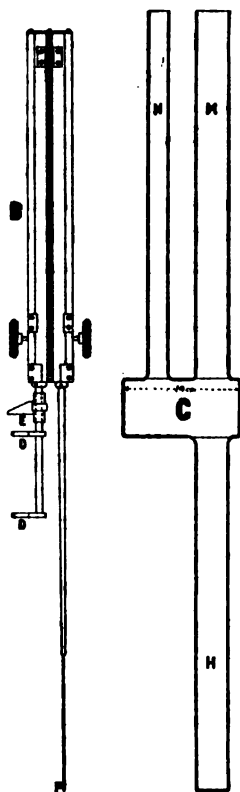


Fig. 4B. Fig. 4C.

The procedure will be described for the case where water is taken as the heavier of the two liquids. In this case the tube C is filled with water until H is completely full and the bulb C¹ is also nearly full, but not so full that the large meniscus which forms strikes the top of this bulb. The capillary tube is steamed out for some time before it is used. This precaution, while seemingly very simple, is essential if the best results are to be obtained, since it puts the surface of the glass in a better condition than cleaning by a cleaning mixture, or the use of acids, alkalies, or organic solvents. Any of these may be used first if it is considered advisable. The capillary tube is then set into the tube M, and lowered by the ratchet screw R, until the top opening in the capillary is underneath the surface of the water, and all of the air is displaced by the water. The upper tubes are then filled with the lighter liquid (*e. g.*, benzene) and after the liquids come to the proper temperature in the thermostat, the capillary tube is raised until the water-benzene meniscus *falls* to one of the graduations on the tube. The point P, which is made of platinum and should be sharp, is lowered until it touches the mirror surface of the benzene-water interface in the bulb C. If the slides in B move with just the right amount of friction this adjustment may be made with extreme accuracy since the point P approaches its image in the interface and the moment the two touch, the water surface gives a slight jump upward. The vertical distance between the platinum point and the graduation on the tube

¹ The bulb C is about 100 mm. in diameter, and has therefore a much larger free liquid surface than has been used in most other work on capillarity.

may then be read off on the millimeter scale by means of the verniers, or a cathetometer may be used to determine the distance. The advantages in the use of this instrument are (1) that it holds the capillary tube firmly in a vertical position, and (2) that the ratchet screws allow the adjustment of the point P to be made with great ease, and also make it easy to lower the capillary tube into the water phase and then raise it until the meniscus is at one of the graduations on the tube. A cathetometer may, of course, be used to measure off directly the distance between the upper and the lower meniscus, and the work recorded here has been checked by measurements made in this way.

The results obtained by the use of this method are much more concordant than the determinations made with a single liquid. This is due largely to the fact that with water-benzene a 1.4 mm. tube could be used and still give a capillary rise of 78 mm., while with water alone in a tube of 2.0 mm. diameter the rise was only about 14 mm., so that, where a considerable height of the capillary column is desirable, a much larger tube may be used for the determination of the interfacial tension. This is advantageous, since not only can the tube be cleaned more readily and the meniscus kept more free from those impurities which easily collect on a small surface and thus vitiate the results, but in addition the diameter of the tube can be determined more accurately.

The Standard Tube.

One difficulty in the determination of the surface tension of a single liquid by the capillary tube method is that the diameter of the tube must, in general, be determined by a mercury calibration, and this is unsatisfactory unless extreme care is taken in the selection of the capillary tube, since it is difficult to find a tube which has the same diameter at different points along its axis, so that the diameter determined by the calibration is usually not that of the tube at the point where the meniscus stands, and in addition the tubes are not round. Two methods of surmounting this difficulty suggested themselves: (1) to use in the place of the tube two plates of optical glass with flat surfaces practically parallel to each other; and (2) to enlarge the hole in a capillary tube by turning it out on a very accurate lathe, and thus make it practically round and of the same diameter for a distance of a few centimeters. This latter alternative, seemingly the more difficult of the two, is the only one which has been used up to the present time. The tube was made in a very skillful way by Captain A. de Khotinsky, the instrument maker for this laboratory, and by whom the eight tips used for the drop-weight method were ground. These tips are sharper and more nearly round than those which may be purchased from the makers of the Morgan drop-weight apparatus, which is, however, used for a different purpose than that described in this paper.

CHICAGO, ILL.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE SURFACE TENSION AT THE INTERFACE BETWEEN TWO LIQUIDS, AND THE EFFECT OF ACIDS, SALTS AND BASES UPON THE INTERFACIAL TENSION.

(SURFACE TENSION III.)

By WILLIAM D. HARKINS AND E. C. HUMPHERY.

Received October 22, 1915.

Only a very few accurate measurements have been made upon the interfacial tension between two liquids. Table I gives the new results which have been obtained by the use of the capillary-tube method. The surface tension at the interface water-benzene between 0° and 40°, is given by the equation

$$\alpha = 35.54 (1 - 0.056t).$$

The effect of acids, bases, and salts upon interfacial tension is of great interest on account of the importance of this effect in relation to colloids, and therefore it is also of great interest in the study of the physiology of plants and animals. It is well known that when a muscle is at rest it gives a neutral reaction, but when it becomes active the reaction changes to acid. One of the theories of muscular motion is that the production of carbonic, lactic, or other acids is caused by a partial decomposition of chemical compounds in the muscles, that this production of acid causes a change in the electromotive force between the fibrilles and the sarco-plasma, and that this in turn causes a change in the surface tension at the boundary between the two phases which is sufficient to account for the motion of the muscles. Experiments by Haber and Klemenciewicz show that this change of electromotive force, if produced in the system benzene-water, is of no small magnitude, but may be nearly as much as one volt for a small change of concentration from basic to acid near the neutral point. Although the relation between the chemical change and the electromotive force at the interface is thus very simple, the relations with surface tension are very much complicated and obscure. The

TABLE I.—SURFACE TENSIONS OF WATER—LIQUID X.

Liquid.	Benzene.					Ethyl car- bonate, 25°.	Di- methyl aniline.	Xylene.	Tolu- ene.	Hex- ane.
	10°.	20°.	25°.	30°.	40°.					
Surf. Tens. (Dynes)	34.98	34.52	34.18	33.82	33.22	13.00	25.78	37.60	36.10	49.54

effect of different concentrations of a number of acids, bases, and salts upon the interfacial tension benzene-water is shown by data given in Table II and in Fig. 5. As will be seen from this table, the inorganic acids have only a small effect upon the interfacial tension, but the organic acids have a considerable effect, which increases with the change from formic toward butyric acid.

The data are given for only one base, ammonium hydroxide. A large number of determinations have been made by the drop-weight method of the effect of highly ionized bases, such as sodium or potassium hydroxide. These bases lower the surface tension slightly, and the results obtained at any one time when the same solution of the base is used, agree well,

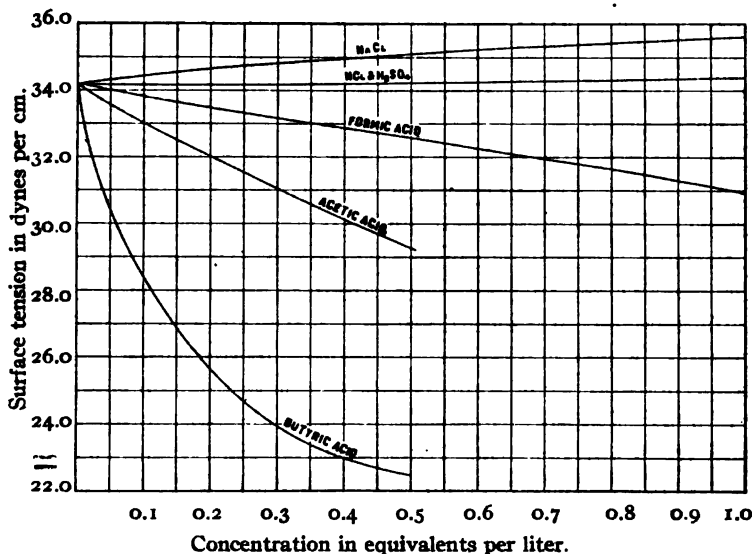


Fig. 5.—Surface tensions at the interface: Aqueous solution—Benzene.

but when different solutions of the base are used, or when the solution has been allowed to stand for some time, the results vary. The capillary-tube method as used by von Lerch,¹ is extremely inaccurate when a highly ionized base is present in the aqueous phase. The work upon the strong bases is still incomplete, and the data obtained will be reserved until later.

TABLE II.—WATER SOLUTION—BENZENE.

Hydrochloric Acid.

Conc., normal.....	0.000	0.0049	0.0098	0.0492	0.0980	0.987
Surface tension	34.18	34.22	34.21	34.17	34.23	34.35

Sulphuric Acid.

Conc., normal.....	0.000	0.0122	0.0242	0.0604	0.1208	0.2416	0.604	1.208
Surface tension ...	34.18	34.16	34.17	34.15	34.15	34.18	34.29	34.39

Sodium Chloride.

Conc., normal.....	0.000	0.0061	0.0123	0.0614	0.1228	0.2507	0.5205	1.034
Surface tension ...	34.18	34.21	34.25	34.33	34.49	34.75	34.99	35.67

WATER SOLUTION—BENZENE.

Formic Acid.

Conc., normal.....	0.00	0.005	0.010	0.0505	0.101	0.1935	0.2525	0.5275	0.881
Surface tension....	34.18	34.19	34.22	34.01	33.84	33.46	33.32	32.49	31.39

¹ *Ann. Physik*, 9, 434-41 (1902).

TABLE II (continued).

Acetic Acid.

Conc., normal....	0.000	0.103	0.492	0.1034	0.2068	0.508
Surface tension...	34.18	34.01	33.56	33.02	31.99	29.24

Butyric Acid.

Conc., normal....	0.000	0.010	0.020	0.100	0.200	0.300	0.500
Surface tension...	34.18	33.01	32.17	28.37	25.63	23.89	22.45

WATER SOLUTION—BENZENE.

Ammonium Hydroxide.

Conc., normal.....	0.000	0.0078	0.390	0.780
Surface tension.....	34.18	34.00	33.25	32.83

Summary of Papers I, II, and III.

1. The capillary tube method of determining surface tension has been found to be inaccurate whenever aqueous solutions of bases are used, but the drop-weight method gives accurate results. The difference is due to the fact that in the capillary tube method the surface of the liquid is very small, which makes it very sensitive to the action of impurities. In this method too, there is always the doubt as to the magnitude of the contact angle. The surface of a drop such as is used in drop-weight determinations is, on the other hand, relatively large, and may also be formed very quickly, thus giving a fresh surface, and the theory of the form of the drop gives no indication that the angle of contact is dependent upon the material of the tip if the tip has the proper form.

2. Lohnstein's theory as to the form of the function which must be inserted in the equation giving the surface tension α in terms of the weight of the falling drop (W), has been tested experimentally at the interface between two liquids. This is an ideal method from the standpoint of the theory of the formation of the drop, since in a liquid the drop falls much more slowly than in a gas. Lohnstein calculated the values of the function of r/a in the equation $\alpha = W[2\pi r f(r/a)]$. When Lohnstein's values of the function are plotted together with the experimental values as in Fig. 1, it is seen that the two curves have exactly the same form, especially at the beginning of the curve where $f(r/a) = 1$, and $r/a = 0$. For the larger values of r/a the experimental curve is smooth, while the Lohnstein curve becomes sinuous. This sinuosity is probably the effect of a failure to carry the integrations to a sufficient completeness, which probably resulted from the extreme laboriousness of a complete calculation. Lohnstein's values are not accurate to a greater degree than 4%, so they cannot be used as a basis for accurate work, but his work has the great value that it proves that such laws as that of Tate are only approximations. The experimental curve is undoubtedly more accurate than that of Lohnstein.

3. The surface tension curve is somewhat flat at the bottom, and Tate's

law assumes that the horizontal tangent is the same as the curve. However, it can be seen from the form of the curve that other tangents can be drawn which approximate the curve as closely as that which is horizontal, so that on this basis laws could be formulated, each as good as that of Tate though not so simple, and as numerous as the tangents to the curve.

4. The correction curve found experimentally is lower than corresponds to the values given by Morgan. This does not mean that Morgan's drop weights are incorrect, but that the values of the surface tension as determined by Ramsay and Shields and other workers by the capillary tube method are too low, since these are the results used by Morgan for the determination of the constant of his equation.

5. The correction factor used in the determination of surface tension by the drop-weight method may be brought very close to the value one by the use of extremely narrow tips, as was done by Antonow, but this is very inadvisable, as his results show, since they vary by 8%.

6. A surface tension apparatus has been devised for the accurate determination of surface tension at a liquid-liquid interface. This apparatus is very simple to set up and easy to use. It can be used for the determination of the surface tension of a single liquid, but the apparatus described in the fourth paper of this series is better suited for this purpose. Another apparatus (Fig. 4), designed for the determination of the surface tension by the capillary tube method, is described. The tube which contained the large meniscus (Fig. 4C) was 10 cm. in diameter, and to check the results the large meniscus was made about 15 centimeters in a glass cylinder. By the use of such large tubes the most common error in capillary height measurements was avoided. The use of a very large lower meniscus, advocated by one of the writers at the Boston meeting of the American Chemical Society, in 1909, and also in this paper as read before the National Academy in December, 1914, is considered by Richards and Coombs to be responsible for a large part of the increase in the values of the surface tension which they find in their work as compared with the older work of Ramsay and Shields and other workers.

7. The surface tension has been determined at the interfaces between water and the following liquids: benzene, ethyl carbonate, dimethyl aniline, xylene, toluene, and hexane. The results at the interface water-benzene are about 6% higher than those obtained formerly by von Lerch or by Antonow. This is interesting in that it is a change in the same direction as that found by Richards and Coombs for the surface tension of single liquids.

8. The effects of acids, bases and salts upon the surface tension at the water-benzene interface, have been studied, and the results are shown graphically in Fig. 5. The effect of bases is much smaller than was found by von Lerch, for example, the new results are in some cases as much

as 35% higher than the older ones. The difference in the results is due to a change from the capillary tube to the drop-weight method.

CHICAGO, ILL.

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

A SIMPLE APPARATUS FOR THE ACCURATE AND EASY DETERMINATION OF SURFACE TENSION, WITH A METAL THERMOREGULATOR FOR THE QUICK ADJUSTMENT OF TEMPERATURE.

BY WILLIAM D. HARKINS AND F. E. BROWN.¹

Received November 10, 1915.

The importance of the values of the surface tension of a liquid in connection with work in colloidal chemistry, on molecular association, and such technical work as the testing of soap, makes it important to devise apparatus for the determination of the capillary constant which is at the same time easy to use, and capable of giving very accurate results. The aim of the designers of the apparatus here described has been to construct an apparatus as easy or easier to use than the stalagmometer of Traube, or of Donnan, and also so well designed that it will give results of the highest accuracy.

The new apparatus has the following advantages: The surface tension tips are very perfectly ground, and are made from Jena glass, monel metal, or quartz; no cement is used in setting in the tip, so the danger of contamination is eliminated; the apparatus is very rigid; one tip may be taken out, and another one substituted in less than five minutes; the apparatus is already provided with a leveling arrangement which is extremely easy to set, and it is not fragile. Perhaps the greatest advantage over the Morgan² apparatus lies in the substitution of a metal construction for glass, and the consequent elimination of cements, amalgams, linseed oil and plaster of Paris mixtures, and wooden or glass blocks. The setting of these requires a great amount of time, and this is apt to discourage the worker from replacing one surface tension tip by a more suitable one. In the new apparatus the weighing bottles are protected from the water of the thermostat by a nickel plated brass box, fastened to its top by thumb screws, and with a joint made waterproof by a rubber gasket, R (Figs. 1 and 2). In the apparatus as described, monel metal stoppers are used but glass stoppers may be substituted for these if a slight change is made in the design, as indicated in the last part of the paper.

¹ This is the first of a series of papers on surface tension to be presented to the University of Chicago by F. E. Brown as a dissertation in part fulfillment of the requirements for the Ph.D. degree.

² THIS JOURNAL, 33, 349 (1911).

Description of the Apparatus.

The fundamental requirements of a first-class drop-weight apparatus are that the glass or metal tip from which the drop is suspended must be as nearly as is possible a perfect circle, and that the edges of the tip must be sharp.¹ Above the tip the glass capillary is ground to fit into a monel metal stopper, which in turn fits into the weighing bottle into which the

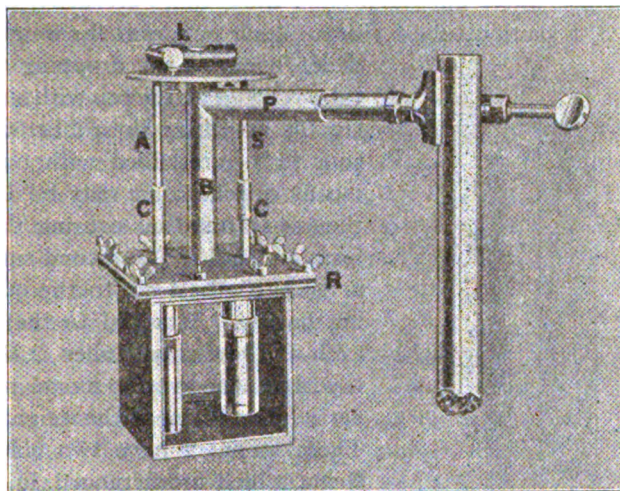


Fig. 1.

drops are caused to fall. This glass capillary tube is bent in the shape of an inverted U, and the other limb of this tube is inserted through a second monel metal stopper and passes down into a second weighing bottle which contains the liquid whose surface tension is to be determined.

The two weighing bottles with their two monel metal stoppers and the dropping tube and tip are supported inside of a rectangular metal box about 10×12 cm. of nickel plated brass, with two large glass windows on opposite sides so that the interior may be easily observed. The apparatus is kept supported in a water filled thermostat during a measurement, and this outer box is necessary to keep the weighing bottles dry. The apparatus is supported by an arm, P, which is a part of the column B. The arm is hollow and slides on the rod of the suitable laboratory support which should have a tripod base with 3 leveling screws. The vertical rod of this support should be at least 30 mm. in diameter.

The top part of the column B terminates in a circular platform with two leveling screws and a resting point on which the cross level L is placed.

¹ The glass tips ground by the instrument maker of this laboratory, Captain A. de Khotinsky, are much more perfect than the writers had been able to obtain from any other source.

The level, by means of the two leveling screws, can be easily set parallel to the drop surface of the surface tension tip D, thus insuring a correct position of the tip whenever the instrument is leveled by means of the screws in the base of the support. Two tubes, C, C', are placed in the cover and these are made of sufficient length to prevent leakage of water from the constant temperature bath into the apparatus when this is submerged 5 cm. below the water line. Through these tubes are fitted two smaller tubes, one, S, a suction tube for drawing air out from the weighing bottle

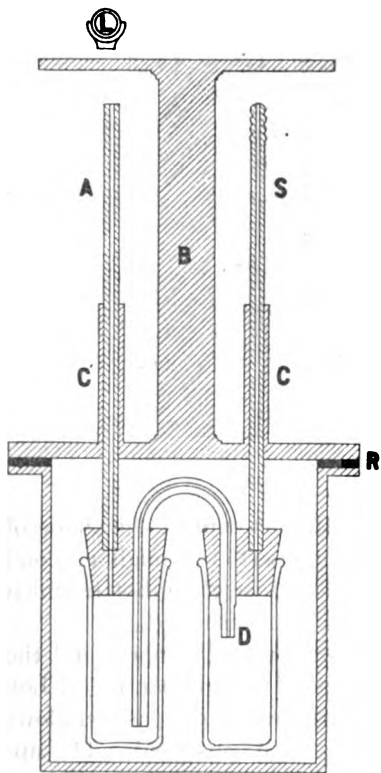


Fig. 2.—Drop-weight apparatus.

which contains the dropping tip. This tube is fitted at the top with a corrugated tip for attaching the rubber tube which runs to a buret filled with mercury, by means of which air may be drawn from the apparatus, thus causing the drop to form and fall. The second small tube A is used to admit air to the other weighing bottle. Attached to the bottom of each of these small tubes is the slightly tapering noncorrosive monel metal stopper which fits one of the weighing bottles. These stoppers have two holes through them, which are arranged in the same way as in a two-hole rubber stopper as sold commercially, except that the hole which carries the tip is as close to the center as is possible. One of these holes is attached to the small metal tube just described, and into the other is fitted the glass capillary tube which carries the tip.

To set up the apparatus and make a surface tension measurement the box is removed from its cover. This is easily done by loosening the thumb screws (Fig. 1) at the top which hold it tight against a rubber gasket. The ground tip of the U tube is then inserted in the stopper to which the suction tube is attached. The joint is air-tight. The top of the suction rod S is then pushed up through the tube C until the top bend of the surface tension tube nearly touches the cover of the apparatus. The atmospheric tube A with its attached monel metal stopper, is inserted in the tube C' in such a way that the other arm of the surface tension tube passes through the second hole of the stopper. The eccentric arrangement of the supporting tube and the second hole in the stopper makes it easy to accommodate any inaccuracies in the bending of the surface tension tube.

To level the surface tension tip, a square cover glass is moistened with glycerine and placed on the ground tip. Then the apparatus is adjusted so that when the cover slip is viewed from one corner through the cathetometer telescope, the three visible corners are in a straight line. Now the leveling screws are so manipulated that both bubbles of the cross level rest at zero, and then they are clamped in this position.

A weighing bottle, which fits the stopper provided with the atmospheric tube, is filled about two-thirds full of the liquid whose surface tension is to be measured and set on the stopper. Friction alone will easily hold it if it is properly ground,¹ and this is very easily done, since the sides of the stoppers are made at a very slight angle in order to give a long line of contact. One advantage of the monel metal stoppers is that they are so hard that a large number of weighing bottles may be ground on one stopper without any appreciable effect upon the stopper. Another weighing bottle is weighed with its glass stopper, and is then fitted on the monel metal stopper which carries the surface tension tip. A rubber tube is attached to the suction tube, and is connected with the special buret used for reducing the pressure.

The modification in the design of the stoppers when they are made from glass, is shown in Fig. 3.

The Control of the Drop.—In the determination of surface tension by the drop-weight method it is very important that the detachment of the drop from the tip shall be as slow as is possible, since in no other way is it possible to obtain a considerable degree of constancy in the weight of the drop, and furthermore, the simple theory developed by Lohnstein for the correction of drop-weight results, is based upon the detachment of the drop while it is increasing in size at only an infinitesimal rate.

The apparatus which has been developed for the control of the drop is extremely simple, and consists of a dropping tube (Fig. 4) fitted with three stopcocks. The tube is filled with mercury by means of the funnel C, and is attached to the suction tube of the drop-weight apparatus by a rubber tube connected at A. When it is desired that a drop be formed, the stopcocks B and E are opened and D is closed. The mercury then

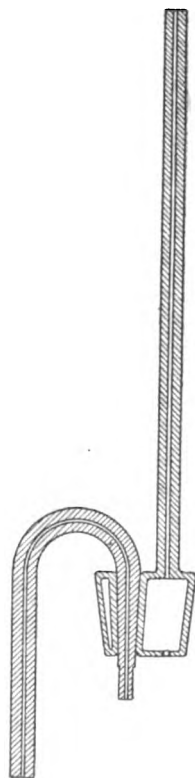


Fig. 3.—Glass stopper, tip tube, and suction tube for drop-weight apparatus.

¹ Thus an experiment showed that a weight of 1100 g. was held up in this way when the weighing bottle was set on only moderately tight, so that it could be taken off with a fair degree of ease. There is therefore no need of any other support.

runs in a stream from the very fine tip of the tube at F. When enough mercury has been run out to cause the drop to form rather rapidly, the

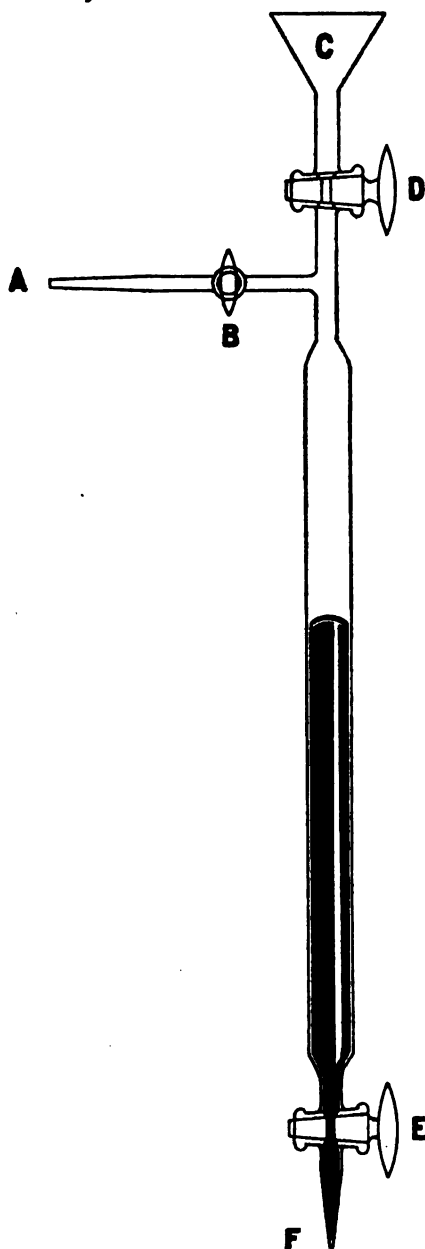


Fig. 4.—Apparatus to control the formation of drops.

stopcock E is closed. The correct amount to run out depends upon the size of the drop. When the drop is fully formed and ready to fall, which condition is readily recognized by an experienced worker, the stopcock D is opened to bring the apparatus to atmospheric pressure, and then it is closed. The speed of formation of the drop is thus reduced to practically zero in a very short time. Then the stopcock E is rotated half way round rather rapidly, thus allowing a very small amount of mercury to escape through the fine opening F. The extremely slight reduction of pressure which results, is sufficient under these circumstances, to cause the drop to detach itself from the tip as slowly as is possible.

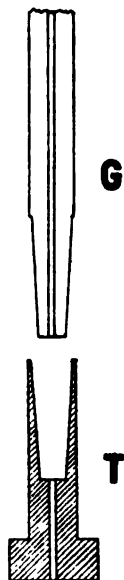


Fig. 5.—Interchangeable metal tips for drop-weight apparatus.

Interchangeable Monel Metal Tips.—Fig. 5 shows a monel metal tip, T, and the method of holding it on the glass tip-holding tube G. The glass tube is ground exactly to fit the monel metal tip, and with such a slight angle that friction holds on the tip very firmly. Any number of tips of different sizes may

be turned to fit the one glass tube. The tip depicted in the figure is 2 cm. in diameter, and is for use in the apparatus designed by Harkins and Humphrey for the determination of the surfacetension at the interface between two liquids. When used with the apparatus described in this paper the tip is made shorter. These shorter tips may be used in either form of the apparatus.

When such large tips are used the liquid will not completely wet the tip unless the bottom is made with a fine grain. If the grain is coarse the diameter of the tip is affected but with large tips it should not be made too fine, or the liquid will not spread over it. To prevent spreading the vertical sides of the tip are always made with a high polish.

The Thermoregulator.—In some surface tension work it is desirable to have a thermostat whose temperature may be varied as rapidly as possible, and with a thermoregulator which is accurate, and which can also be set at once to regulate to any temperature within the range for which it was designed.

The regulator used in this laboratory for this purpose (Fig. 6) was designed by Captain de Khotinsky, and possesses a number of advantages over the usual thermoregulator. In order to reduce the lag, and make it respond quickly to changes of temperature, it is made from nickel plated steel and is filled with mercury. The great advantage of the steel tube is that steel has about 66 times the thermal conductivity of glass. While ordinary steel has a higher coefficient of expansion than glass, steels high in nickel have a lower coefficient, and steels have been made even with a negative coefficient. Toluene, which is often used to fill thermoregulators, is about sixty times as poor a conductor of heat as mercury.

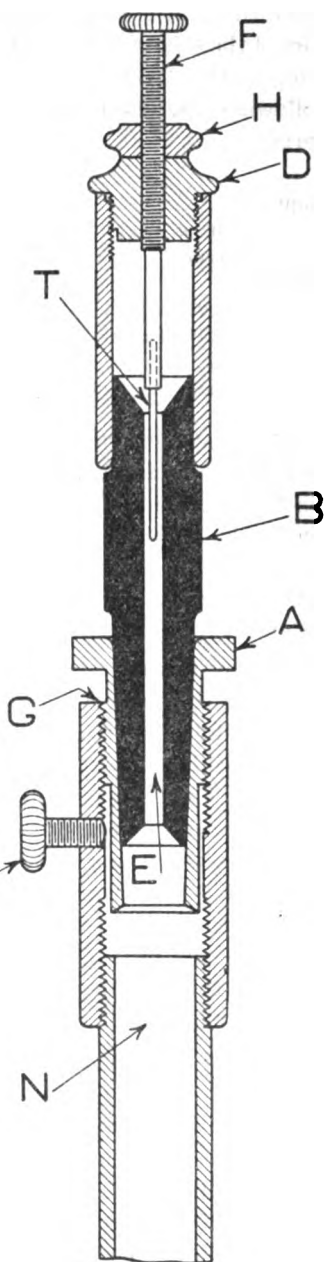


Fig. 6.—Metal thermoregulator.

Its supposed advantage comes from the fact that it has about twice as great a coefficient of expansion, but this is not an advantage after all, since the heat is conducted through the toluene so slowly that only a thin film of the toluene next to the material of the regulator, changes its temperature, so the effective expansion is usually less than that of mercury. The following approximate data make it easy to compare these different materials.

	Linear coefficient of expansion.	Thermal conductivity.
Liquids:		
Toluene.....	0.000366	0.000307
Mercury.....	0.000182	0.0177
Solids:		
Soft glass.....	0.0000094	0.0015
Jena hard glass.....	0.0000073
Iron.....	0.00000118
Nickel steel, high in Ni.....	0.0000050	0.100

At the suggestion of one of the writers Captain de Khotinsky has provided this thermoregulator with a glass capillary tube, B, which makes visible the contact between the platinum point and the small mercury meniscus. This capillary is ground to fit exactly the metal parts, and this gives the advantage that the platinum contact point is exactly centered, which is very important.

This regulator can be set very quickly at any temperature from 1° to 97° by turning the regulating screw A. For the more delicate adjustment the screw F is turned and the check nut H is set. The apparatus may be filled by releasing the set screw K, unscrewing the thermoregulating head-screw A, and adding mercury up to within 10 mm. from the top G. The regulating head-screw is then replaced and turned until the milled head A comes to within 1 mm. of the shoulder G. Next the cap D is unscrewed and all the mercury above the capillary glass tube B is removed. The meniscus is brought into the proper position in the capillary by turning the head-screw A. The capillary may be cleaned by unscrewing the head-screw, and pushing a small ball of absorbent cotton through the capillary. It is important that the hollow cones at E and T be cut into the top and bottom of the capillary tube.

At N is screwed on the steel tube containing the greater part of the mercury. When a very delicate regulation of the temperature is desired, several tubes joined together at the top are substituted for this one tube.

The writers wish to express their indebtedness to the Warren Fund of the American Academy of Arts and Sciences for financial aid in the development of the surface tension apparatus.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF VIRGINIA.]

THE DIFFUSION OF IODINE IN POTASSIUM IODIDE SOLUTIONS.¹

BY GRAHAM EDGAR AND STERLING H. DIOGS.

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A few years ago a series of papers appeared in the *American Journal of Science*, by Van Name and his co-workers,² dealing with the rates of reaction of metals with halogens dissolved in solutions of metallic halides. In these papers it was shown that numerous metals react with a given solution of, say, iodine dissolved in potassium iodide solution, at a rate which is independent of the nature of the metal. This is in harmony with the diffusion theory of heterogeneous reaction,³ according to which the rate of such reactions is determined by the rate of diffusion of the iodine to the metal and is independent of the metal. In the above papers, however, a fact was brought out which seemed to merit further investigation. This was the unexpected result that the rate of reaction of iodine with metals was markedly influenced by the concentration of the potassium iodide in which the iodine was dissolved, an increase in the concentration of the potassium iodide producing a marked increase in the rate of the reaction. This would be in accord with the diffusion theory only if iodine *diffuses* more rapidly in a concentrated solution of potassium iodide than in a dilute one. No reliable data on this point were available, and the present paper deals with the experimental investigation of the subject.

Apparatus and Technique.

The first determinations were made in a diffusion cylinder similar to that employed by Scheffer,⁴ and Stefan,⁵ using a four-layer system, and calculating the diffusion constant with the aid of the tables of Stefan. This method proved unsatisfactory in the case of the solutions investigated, partially because of the very slight difference in specific gravity of the layers, and partially because of the length of time necessary for the completion of a single experiment (about 8 days), during which any variation of temperature, or any jarring would cause a complete loss. The method finally employed was a two-layer system, and the method of employing it will be described in some detail. Glass diffusion cylinders were used, of a capacity about 35 cc., and a length about 8 cm. They

¹ The data given in this paper are taken from *Bull. Philosophical Soc.*, University of Virginia, Scientific Series, Vol. 1, pp. 477-512 (1914).

² Van Name and Edgar, *Am. J. Sci.*, 29, 237; Van Name and Bosworth, *Ibid.*, 32, 207; Van Name and Hill, *Ibid.*, Jan., 1914.

³ Nernst and Brunner, *Z. phys. Chem.*, 47, 52 and 56; Van Name and Edgar, *loc. cit.*

⁴ *Z. physik. Chem.*, 2, 390.

⁵ Wiener, *Akad. Ber.*, 79, 161.

were made with very flat bottoms and true cylindrical sides. These cylinders were fitted with tightly fitting corks, through which passed a separatory funnel terminating in a fine capillary, and a bent capillary tube through which to remove the layers. Fig. 1 is self explanatory. A determination was carried out as follows: The cylinder was rigidly

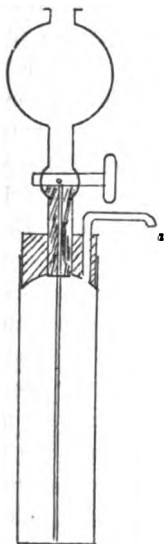


Fig. 1.—Diffusion cylinder.

supported in a sensitive thermostat and allowed to reach the temperature of the bath (usually 25°). About 15 cc. of pure potassium iodide solution was then carefully introduced through the separatory funnel and run into the cylinder. After a few minutes, exactly the same amount of a solution of iodine in potassium iodide was introduced in the same way, being run in under the first layer. The concentration of potassium iodide in the two layers was identical. After three or four days the two layers were removed for analysis. This was accomplished by very carefully running a concentrated solution of potassium iodide into the cylinder under the two layers and gradually raising the level until the top layer had just appeared at the mouth of the exit tube at *a*. Any liquid remaining in the separatory funnel was then carefully removed with a roll of filter paper, and an amount of concentrated potassium iodide solution exactly equal to the volume of the first layer was measured into the funnel and run into the cylinder, thus displacing at *a* the liquid in the top layer. This was then analyzed for iodine by titration with dilute sodium thiosulfate solution. The iodine in the bottom layer was determined by subtracting that in the top layer from the total amount originally introduced (also determined by titration). The diffusion constant is calculated from these data with the aid of the following formula:

$$K = \frac{r^2}{t} \frac{2.30}{\pi} \log \frac{8}{\pi^2} \frac{V_0}{V_0 - V_1}$$

where *r* is the total length of the liquid column in the cylinder; *t* the time of diffusion, in days; *V*₀ the total amount of iodine in the cylinder, and *V*₁ the iodine in the top layer. The derivation of this formula is given in full in *Bull. Philosoph. Soc.*, U. Va., referred to above.

Even with the improved method, numerous determinations came to grief through accidental errors of technique, fluctuations of the thermostat temperature caused by breaks in the city electric current, vibration of the building, and other sources. The tables give all of the results which the authors believe to be free from other than average experimental error. In all cases duplicate results were obtained, usually four cylinders being run at the same time. This is quite necessary, as a two-layer

system gives no check with the lower layer, while the four-layer system should give three checks on each determination.

In addition to the diffusion data, the fluidity of the potassium iodide solutions used was measured for purposes of comparison. The measurements of fluidity were carried out in the usual Ostwald viscosity tube, no especial care being taken to achieve the highest degree of accuracy, since the purpose of the measurements was purely for comparison.

The diffusion of iodine (about 0.05 *N* in all cases) was measured in potassium iodide solutions of concentrations 0.25 *N*, 0.5 *N*, *N*, 2 *N*, 3 *N*, and 4.5 *N*. The fluidity of all of the potassium iodide solutions was also measured. The results follow.

TABLE I.—DIFFUSION OF IODINE IN POTASSIUM IODIDE SOLUTION (25°).

Normality of KI_2 , $\frac{1}{10}$. Normality of KI , 0.25.

* I.	P.	l. (length of liquid layer). Cm.	P.	t. (time in days).	V. (vol. of $Na_2S_2O_3$ equiv. to it in both layers), cc.	V. (vol. of $Na_2S_2O_3$ equiv. to it in top layer), cc.	K @ 25° (diffusion constant).
c	7.60	58.0	3.70	49.05	14.40	1.083	
d	7.57	57.3	3.70	49.05	14.50	1.080	
e	7.57	57.3	3.70	49.05	14.50	1.080	

Mean, 1.08

TABLE III.—DIFFUSION OF IODINE IN POTASSIUM IODIDE SOLUTION.

Normality of KI_2 , $\frac{1}{10}$. Normality of KI , 1.

* I.	P.	l.	P.	days.	V.	V.	Temp.	K.	K @ 25°.
a	7.54	56.9	3.72	26.20	8.18	25.0°	1.20	1.20	
b	7.56	57.2	3.73	26.20	8.18	25.0°	1.19	1.19	
a	7.54	56.9	4.01	26.50	8.51	24.8°	1.175	1.18 ¹	
b	7.56	57.2	4.02	26.50	8.54	24.8°	1.183	1.19 ¹	
c	7.60	58.0	4.02	26.50	8.52	24.8°	1.194	1.20 ¹	

Mean, 1.195

TABLE II.—DIFFUSION OF IODINE IN POTASSIUM IODIDE SOLUTION (25°).

Normality of KI_2 , $\frac{1}{10}$. Normality of KI , 0.5.

*	I.	P.	t.	V _o .	V _i .	K.
a'	7.48	56.2	3.68	39.00	11.80	1.10
e	7.57	57.3	3.69	39.00	11.50	1.09
d	7.57	57.3	3.75	39.40	11.70	1.07
e	7.57	57.3	3.75	39.40	11.70	1.07
c	7.60	58.0	3.73	42.00	12.40	1.07
d	7.57	57.3	3.73	42.00	12.50	1.08
e	7.57	57.3	3.73	42.00	12.50	1.08

Mean, 1.08

TABLE IV.—DIFFUSION OF IODINE IN POTASSIUM IODIDE SOLUTION (25°).

Normality of KI_2 , $\frac{1}{10}$. Normality of KI , 2.

*	I.	P.	l.	Vo.	V ₁	K @ 25°.
a'	7.48	56.2	2.94	35.32	10.20	1.25
c	7.60	58.0	2.94	35.32	10.15	1.26
d	7.57	57.3	2.94	35.32	10.26	1.27

Mean, 1.26

* Asterisk refers to the particular cylinder used.

¹ Calculated by extrapolation, with the aid of the formula of Nernst.

TABLE V.—DIFFUSION OF IODINE IN POTASSIUM IODIDE SOLUTION (25°).

Normality of KI ₂ , 1/30.		Normality of KI, 3.		Vi. K @ 25°.	
* I.	P.	I.	Vo.		
c	7.60	58.0	3.21	48.30	14.30 1.255
a'	7.48	56.2	3.74	48.60	15.85 1.285
c	7.60	58.0	3.74	48.60	15.75 1.300
d	7.57	57.3	3.74	48.60	15.50 1.250
a'	7.48	56.2	3.06	48.90	14.45 1.275
c	7.60	58.0	3.06	48.90	14.30 1.286
d	7.57	57.3	3.06	48.90	14.30 1.275
e	7.57	57.3	3.06	48.90	14.30 1.275
a'	7.48	56.2	2.92	51.00	14.95 1.268
Mean, 1.275					

TABLE VI.—DIFFUSION OF IODINE IN POTASSIUM IODIDE SOLUTION (25°).

Normality of KI ₂ , 1/30.		Normality of KI, 4.5.		Vi. K @ 25°.	
* I.	P.	I.	Vo.		
a'	7.48	56.2	3.15	44.75	13.50 ¹ (1.29)
					1.28
c	7.60	58.0	3.15	44.75	13.20 1.27
d	7.57	57.3	3.15	44.75	13.30 1.27
Mean, 1.275					

¹ In this case 2 drops too much were drawn off with the layer titrated. Making the correction, we obtain the unbracketed value for K given above.

TABLE VII.—FLUIDITY OF POTASSIUM IODIDE SOLUTION.

Normality. KI.	Time of flow.	Fluidity (rel. 25°).	Density.
0.125	44.4	1.010	1.0125
0.250	43.8	1.010	1.0275
0.500	41.8	1.025	1.0580
0.750	40.2	1.035	1.0890
1.000	38.6	1.050	1.1180
1.500	36.2	1.060	1.1760
2.000	34.2	1.070	1.2360
2.500	32.6	1.070	1.2950
3.000	31.4	1.070	1.3520
3.500	1.060	1.4165
4.000	1.042	1.4680
4.500	1.020	1.5260
5.000	0.996	1.5830

TABLE VIII.

Normality. KI.	Fluidity (rel. 25°). KI.	Diff. const. I ₂ in KI.	React. vel. constants. ¹
0.250	1.010	1.080
0.500	1.025	1.080
0.600	8.75
1.000	1.050	1.195
1.200	9.58
2.000	1.070	1.260
2.400	10.15
3.000	1.070	1.280
4.500	1.020	1.280

¹ Mean for Hg, Cu, Cd, and Zn.
Taken from Van Name, Edgar, *loc. cit.*

Discussion of Results.

Tables I to VI contain diffusion data for iodine diffusing in KI solutions 0.25 N, 0.5 N, N, 2 N, 3 N and 4.5 N. Table VII contains measurements of fluidity of KI solutions. Table VIII contains a summary of the data obtained, and a comparison of the rates of diffusion and of reaction of iodine solutions, with their fluidity.

(1) **The Relation of the Reaction Velocity of Iodine Solutions to Their Rates of Diffusion.**—A brief survey of Table VIII shows that the results obtained for the rate of diffusion of iodine in solutions of KI of different concentrations are quite in accord with the results for reaction velocity of these solutions obtained by Van Name and his co-workers. The rate of diffusion increases with the concentration of the KI during the range of concentrations through which Van Name worked, and furthermore, the amount of in-

crease is distinctly of the same order of magnitude as the increase in the velocity constants, so that we can say that the results are thoroughly in accord with the diffusion theory of heterogeneous reactions, insofar as this theory applies to the reaction between iodine solutions and the metals studied by Van Name.

(2) **The Reasons for the Influence of KI on the Rate of Diffusion of Iodine.**—This subject must be considered much more carefully, and will be treated under several heads.

(a) **The Condition of the Dissolved Iodine.**—The work of Leblanc and Noyes,¹ Jakowkin,² A. A. Noyes³ and others has shown that practically no iodine is present as such in potassium iodide solutions, practically all of it combining with the KI to form KI_3 . In solutions containing a large excess of KI, such as were dealt with in this investigation the free iodine in the solution may be neglected, as having no influence on the change in the rate of diffusion.

KI_3 in dilute solution is probably largely dissociated into K^+ and I_3^- , and this dissociation must necessarily be somewhat less in the concentrated solutions of KI than in the more dilute ones, due to the effect of the excess of the common K ion. We are therefore dealing with the diffusion of KI_3 and I_3^- ions, and not with free iodine.

(b) **The Influence of KI on the Diffusion of KI_3 and I_3^- .**—Concerning the influence of KI on the rate of diffusion of undissociated KI_3 we can say very little, though it seems most probable that it must be indirect—as for example, by influencing the fluidity of the solution, a factor which will be treated later. Concerning the actual rate of diffusion of undissociated KI_3 as compared with that of I_3^- ions and K^+ ions, we can only say that, in general, the rate of diffusion of an un-ionized molecule is considerably less than that of its ions. Any increase in the relative amount of KI_3 in the more concentrated KI solutions would therefore have the effect of *decreasing* the total rate of diffusion of the iodine, all other forces being equal.

The influence of KI on the rate of diffusion of I_3^- ions may be discussed according to the principles laid down by Abegg and Bose⁴ on the subject of the influence of a common ion on the rate of diffusion of an electrolyte. The authors show that for many substances the rate of diffusion of an electrolyte is *decreased* by the addition of an electrolyte containing a common ion *if the common ion is the faster of the two*, and *increased* if the common ion is the *slower* of the two. In our case the common K^+ ion with its migration velocity⁵ of about 74.8 is much faster than the I_3^-

¹ *Z. physik. Chem.*, 6, 401.

² *Ibid.*, 20, 19.

³ *Ibid.*, 27, 357.

⁴ *Z. physik. Chem.*, 30, 545.

⁵ Bray and MacKay, *THIS JOURNAL*, 32, 914 (1910).

ion with its migration velocity of about 41.0, so that the influence of increasing the concentration of the KI should *decrease* that rate of diffusion of the I_3^- , if Abegg and Bose's theory be correct.

(c) **The Influence of the Fluidity of the Solution.**—That fluidity has a marked effect upon rates of diffusion is well known, and since solutions of potassium salts in general have high fluidity, it might be expected that this influence alone would account for the observed increase in the rate of diffusion of the iodine with increasing KI concentration. An examination of Table VIII, however, will show that this is not the case. The fluidity of 0.25 *N* KI is 1.010 at 25°, and this increases steadily until a maximum is reached at about 2.5 *N*, where the value is 1.070. After this the fluidity drops rapidly, so that at 4.5 *N* the value is 1.020, and at 5 *N* only 0.996. On the other hand, the diffusion constant rises much more rapidly and becomes uniform at about 2.5 *N*. The value of the diffusion constant at 3 *N* is nearly 20% higher than that at 0.50 *N*, while the corresponding rise in the fluidity curve is only about 5%. A still more striking illustration of the fact that fluidity alone will not account for the increasing diffusion rate is found by comparing the figures for fluidity and diffusion in concentrations of KI 0.5 *N*, and 4.5 *N*. The fluidities are almost *identical*, the more dilute solution being slightly higher, while there is an *increase* in the diffusion constant of almost 20%. It is thus obvious that the effect of increasing KI concentration on the rate of diffusion of iodine cannot be explained by the increase in fluidity alone. Recapitulating, we may say that factors *b* and *c*, treated above, seem entirely inadequate to explain the *increase* in the rate of diffusion of iodine with increasing KI concentration which is shown in Tables I to VII. Factor *b* should work in the opposite direction, if at all, and factor *c* seems entirely inadequate to account for the results. The authors do not, at the present time, attempt to offer any explanation for the observed facts. It would be interesting to investigate other metallic iodides in a similar way, and perhaps sufficient data might be obtained in this way to enable a sound theory to be advanced to account for the facts given in this article.

Summary.

1. The rate of diffusion of iodine dissolved in potassium iodide solutions of different concentrations has been measured at 25°. Increase in the concentration of the KI causes, in general, a marked increase in the rate of diffusion of the iodine. The fluidity curve of KI has also been determined at 25° for a wide range of concentration.

2. The results bear on the work of Van Name and others on the rate of solution of metals in iodine solutions, and entirely corroborate the conclusions of these writers that these reactions are governed by the rate of diffusion of the iodine, under the conditions of their experiments.

3. No satisfactory explanation of the influence of the KI on the diffusion of iodine, is offered, though several possible explanations are considered.

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[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE DENSITIES AND CUBICAL COEFFICIENTS OF EXPANSION OF THE HALOGEN SALTS OF SODIUM, POTASSIUM, RUBIDIUM AND CESIUM.

BY GREGORY PAUL BAXTER AND CURTIS CLAYTON WALLACE.

Received November 15, 1915.

For purposes of computation in the preceding paper upon "Changes in Volume upon Solution in Water of the Halogen Salts of Alkalis" it was necessary to know the densities of the solid salts at different temperatures. Since neither these values nor the coefficients of expansion of the salts have been found with accuracy, the problem of determining the densities over the necessary range in temperature, and thus the coefficients of expansion, was undertaken.

The method employed was that of displacement of toluene. In order to reduce the effect of the errors of experiment, a very considerable quantity of salt was used. Furthermore, especial pains were taken, first in drying the salt, and second, in freeing it as far as possible from entangled air when immersed in toluene in the pycnometer.

The pycnometer itself, instead of being of the ordinary stoppered form for solids, was merely a 25 cc. graduated flask, the neck of which was very much constricted at one point to increase accuracy in adjusting the volume of its contents. The diameter of the constriction was about 2.5 mm. which secured an accuracy in setting of about 0.3 mg. of toluene. This form of pycnometer has the advantages, first that the ground surface is not wet with liquid and hence there is no difficulty from evaporation, second that the neck of the flask serves as a reservoir when used at low temperatures.

The volume of the flask at different temperatures was found by weighing it full of water after the liquid had been set at the mark in the thermostats used for finding the densities of the solutions in the preceding paper. The neck of the flask was dried before the meniscus was set. Preparatory to being weighed, the outside of the flask was washed with dilute ammonia solution, wiped with a clean, slightly damp, cotton cloth, and was allowed to stand in the balance room for at least one hour. In order to find the densities of the different specimens of toluene, the flask was weighed after being filled with toluene at the temperatures used. No attempt was made to purify the toluene beyond drying it over metallic sodium for

some time and distilling without fractionation. In computing the volumes of the flasks the assumption is made that an "apparent" gram of water occupies

1.02378 cc. at 70.19° 1.01315 cc. at 50.04° 1.00400 cc. at 25.00° 1.00119 cc. at 0.00°.

The weights were carefully standardized to tenths of a milligram and the thermometer readings were corrected by comparison with a standard thermometer as described in the preceding paper. The weights of toluene are corrected to the vacuum standard by adding 0.00126 g. for each gram of substance.

TABLE I.
Densities of Toluene Samples.

Temperatures.	70.19°.	50.04°.	25.00°.	0.00°.
Apparent wt. of water.....	24.3184	24.5605	24.7671	24.8186
Volume of flask I.....	24.8994	24.8838	24.8662	24.8482
Wt. of toluene I in vac.....	20.3888	20.8746	21.4661	22.0473
Density of toluene I ref. to water at 4°.....	0.81885	0.83888	0.86327	0.88728
Wt. of toluene II in vac.....	20.8488	21.4222	21.9848
Density of toluene II ref. to water at 4°.....	0.83784	0.86150	0.88477
Apparent wt. of water.....	48.407	48.892	49.299	49.406
Volume of flask II.....	49.563	49.535	49.495	49.465
Wt. of toluene III in vac.....	40.538	41.478	42.616	43.741
Density of toluene III ref. to water at 4°.....	0.81790	0.83734	0.87100	0.88428

Coefficients of Expansion of Flasks and Toluol.

Temperature interval.	70.19°-50.04°.	50.04°-25.00°.	25.00°-0.00°.
Flask I.....	0.0431	0.0428	0.0429
Flask II.....	0.0435	0.0429	0.0428
Toluene I.....	0.001198	0.001144	0.001098
Toluene II.....	0.001114	0.001066
Toluene III.....	0.001167	0.001113	0.001066

It is noticeable not only that the density of Sample I of toluene is markedly higher than those of the other two samples, but also that the coefficient of expansion of this sample is highest, although the change in coefficient of expansion with change in temperature is the same for all three samples.¹ The coefficients of expansion of the flasks are discussed in the preceding paper.

The salts² were purified as described in the preceding paper. In the case of potassium chloride, potassium iodide and rubidium iodide the specimens of salt used in the duplicate determinations were prepared at different times. They were thoroughly dried by fusion—the chlorides

¹ In Landolt-Börnstein, *Tabellen*, 1912, the density of toluene at 0° referred to water at 4° is given as 0.8845 and its cubical coefficient of expansion at 20° as 0.001099. This value for the density corresponds closely to those found for Samples II and III but the above value for the cubical coefficient of expansion is almost identical with that found for Samples I.

² Professor H. L. Wells of Yale University very kindly loaned us very pure cesium material. See a preceding paper.

in platinum crucibles in air, the bromides and iodides in a platinum boat contained in a porcelain tube in a current of pure, dry electrolytic hydrogen. Portions of the fused salts after solution in water were found to give essentially neutral solutions.

Since, almost invariably, fused salts contain cavities, owing probably to contraction during cooling, all of the salts were ground in an agate mortar before use and the powdered material was again dried at 250° in an air-bath and preserved in a desiccator until used.

A series of experiments was carried out as follows: The dried salt was transferred to a clean, dry flask which was weighed with its contents. Toluene sufficient to cover the salt was then added and the flask was exhausted until the toluene boiled gently. The boiling was allowed to continue several moments in order to ensure removal of air from the interstices. Next the flask was nearly filled with toluene and brought to constant temperature in the thermostat, at the highest temperature employed. After it had been brought to room temperature, it was cleaned, dried and weighed as described above. The operations were then repeated at lower temperatures successively.

Vacuum corrections were computed from the densities as finally determined and are employed in the tables as follows:

NaCl + 0.00042	NaBr + 0.00025	NaI + 0.00019
KCl + 0.00046	KBr + 0.00030	KI + 0.00024
RbCl + 0.00029	RbBr + 0.00022	RbI + 0.00020
CsCl + 0.00016	CsBr + 0.00013	CsI + 0.00013

TABLE II.

Salt.	Temp. ° C.	Wt. salt in vac. Grams.	Wt. toluene displaced in vac. Grams.	Density of toluene ref. to H ₂ O at 4°.	Density of salt ref. to H ₂ O at 4°.	Cubical coeff. of expansion of salt.
NaCl ¹	70.19°	8.6156	3.2782	0.81885	2.1521	0.000088
	50.04	...	3.3524	0.83888	2.1559	0.000103
	25.00	...	3.4410	0.86327	2.1615	0.000126
	0.00	...	3.5255	0.88728	2.1683	0.000060
	70.19	14.0885	5.3586	0.81885	2.1528	0.000109
	50.04	...	5.4830	0.83888	2.1554	0.000124
	25.00	...	5.6271	0.86327	2.1613	
	0.00	...	5.7659	0.88728	2.1680	

¹ Previous determinations of the densities of these salts are as follows:

NaCl: Clarke, "Constants of Nature," 1873, I.....	...	2.06-2.16
Retgers, <i>Z. physik. Chem.</i> , 3, 289 (1889).....	17°	2.167
Krickmeyer, <i>Ibid.</i> , 21, 53 (1896).....	20°/4°	2.174

TABLE II (*continued*).

Salt.	Temp. ° C.	Wt. salt in vac. Grams.	Wt. toluene displaced in vac. Grams.	Density of toluene rel. to H ₂ O at 4°.	Density of salt rel. to H ₂ O at 4°.	Cubical coeff. of expansion of salt.
NaBr ¹	50.04	21.1619	5.5514	0.83784	3.1939	
						0.000119
	25.00	...	5.6910	0.86150	3.2034	
NaI ²						0.000122
	0.00	...	5.8270	0.88477	3.2132	
	50.04	16.5363	3.8217	0.83784	3.6253	
						0.000141
	25.00	...	3.9160	0.86150	3.6380	
						0.000132
	0.00	...	4.0081	0.88477	3.6499	
	50.04	26.7938	6.1686	0.83784	3.6387	
						0.000132
	25.00	...	6.3228	0.86150	3.6507	
						0.000137
	0.00	...	6.4715	0.88477	3.6631	
KCl ³	70.19	16.316	6.748	0.81790	1.9776	
						0.000083
	50.04	...	6.897	0.83734	1.9809	
						0.000139
	25.00	...	7.067	0.86100	1.9878	
						0.000084
	0.00	...	7.243	0.88428	1.9920	
	50.04	17.6589	7.4797	0.83888	1.9806	
						0.000116
Crystals.....	25.00	...	7.6752	0.86327	1.9863	
	50.04	13.6465	5.7972	0.83888	1.9747	
						0.000096
	25.00	...	5.9515	0.86327	1.9794	
	50.04	16.6637	5.0955	0.83784	2.7399	
						0.000125
KBr ⁴						
	25.00	...	5.2231	0.86150	2.7485	
						0.000112

- ¹ NaBr: Schiff, *Ann.*, 108, 21 (1858)..... 2.952
 Kremers, *Jahresb.*, 10, 67 (1857)..... 17.5° 3.079
 Tschermak, *Sitzungsb. d. k. Akad. Wien.*, 45, 603.. 3.011
 Favre and Valson, *Compt. rend.*, 77, 579 (1873).... 17.3° 3.198
² NaI: Schröder, *Ann.*, 192, 295 (1878)..... 3.55
 Füllhol, *Ann. chim. phys.*, [3] 21, 415 (1847)..... 3.45
 Favre and Valson, *Loc. cit.*..... 18.2° 3.654
 Baxter and Brink, *THIS JOURNAL*, 30, 46 (1908)... 25°/4° 3.665
³ KCl: Clarke, "Constants of Nature," 1888, Part I..... 1.836-1.995
 Retgers, *Loc. cit.*..... 16° 1.989
 Krickmeyer, *Ibid.*..... 20°/4° 1.994
 Buchanan, *Proc. Chem. Soc.*, 21, 122 (1905)..... 23.47° 1.951
 Johnston and Adams, *THIS JOURNAL*, 34, 572 (1912)
 Finely powdered..... 30°/4° 1.984
⁴ KBr: Karsten, *Schweig. Jour.*, 65, 394 (1832)..... 2.415
 Playfair and Joule, *Mem. Chem. Soc.*, 2, 401 (1845) .. 2.672

TABLE II (continued).

Salt.	Temp. ° C.	Wt. salt in vac. Grams.	Wt. toluene displaced in vac. Grams.	Density of toluene ref. to H ₂ O at 4°.	Density of salt ref. to H ₂ O at 4°.	Cubical coeff. of expansion of salt.
KI.....	0.00	...	5.3491	0.88477	2.7562	
	50.04	17.3647	4.6717	0.83784	3.1142	0.000113
	25.00	...	4.7901	0.86150	3.1230	0.000120
KI ¹	0.00	...	4.9046	0.88477	3.1324	
	50.04	24.3342	6.5557	0.83888	3.1139	0.000115
	25.00	...	6.7266	0.86327	3.1229	0.000124
RbCl ²	0.00	...	6.8924	0.88728	3.1326	
	50.04	10.8005	3.2409	0.83784	2.7922	0.000082
	25.00	...	3.3255	0.86150	2.7979	0.000111
RbBr ³	0.00	...	3.4061	0.88477	2.8057	
	50.04	25.6918	6.4523	0.83888	3.3402	0.000101
	25.00	...	6.6232	0.86327	3.3486	0.000113
	0.00	...	6.7882	0.88728	3.3581	

Beamer, Clarke's "Constants of Nature," 1888,

Part I..... 12.7° 2.712

Spring, *Ber.*, 16, 2724 (1893)..... 18° 2.704

Schröder, "Dichtigkeitsmessungen," Heidelberg, 1873 .. 2.690

Krickmeyer, *Loc. cit.*..... 20°/4° 2.756Buchanan, *Ibid.*..... 2.679Richards and Mueller, *Z. anorg. Chem.*, 53, 423

(1907)..... 25°/4° 2.73

¹ KI: Boullay, *Ann. chim. phys.*, [2] 43, 266 (1830)..... 3.078-3.104Karsten, *Loc. cit.*..... 2.908Playfair and Joule, *Ibid.*..... 13° 3.048-3.070Filhol, *Ibid.*..... 3.056Schiff, *Ibid.*..... 2.850Buignet, *Jahresb.*, 14, 15 (1861)..... 2.970Schröder, *Loc. cit.*..... 3.077-3.083Spring, *Ibid.*, fused..... 20° 3.012-3.112Buchanan, *Loc. cit.*..... 23.4° 3.043Baxter and Brink, *Ibid.*..... 25°/4° 3.115² RbCl: Schröder, *Ibid.*..... 22° 2.209Buchanan, *Ibid.*..... 22.9° 2.706Archibald, *J. Chem. Soc.*, 85, 776 (1904)..... 2.753Setterberg, *Oefvers Stockh. Förh.*, 39, 23 (1882)..... 2.807³ RbBr: Schröder, *Loc. cit.*..... 2.780Setterberg, *Ibid.*..... 3.358Archibald, *Ibid.*..... 3.282Buchanan, *Ibid.*..... 23° 3.210

TABLE II (continued).

Salt.	Temp. ° C.	Wt. salt in vac. Grams.	Wt. toluene displaced in vac. Grams.	Density of toluene ref. to H ₂ O at 4°.	Density of salt ref. to H ₂ O at 4°.	Cubical coeff. of expansion of salt.
RbI ¹	50.04	12.8305	3.0397	0.83888	3.5409	0.000091
	25.00	...	3.1208	0.86327	3.5490	0.000121
	0.00	...	3.1980	0.88728	3.5598	0.000093
	50.04	24.2498	5.7348	0.83784	3.5429	0.000103
	25.00	...	5.8828	0.86150	3.5512	0.000109
	0.00	...	6.0259	0.88477	3.5604	0.000136
CsCl ²	70.19	26.5871	5.5088	0.81885	3.9520	0.000143
	50.04	...	5.6311	0.83888	3.9607	0.000141
	25.00	...	5.7751	0.86327	3.9742	0.000137
	0.00	...	5.9147	0.88728	3.9884	0.000141
CsBr ³	50.04	24.9973	4.7467	0.83888	4.4177	0.000146
	25.00	...	4.8680	0.86327	4.4329	0.000145
	0.00	...	4.9857	0.86728	4.4486	0.000145
CsI ⁴	50.04	28.7568	5.3696	0.83888	4.4926	0.000145
	25.00	...	5.5056	0.86327	4.5090	0.000145
	0.00	...	5.6384	0.88728	4.5253	0.000145

As is to be expected from the greater care taken in preparing the salts free from moisture and from cavities, the foregoing density values tend to be higher than the results of earlier determinations, although it is by no means certain that the second difficulty was entirely eliminated. Most of the results need little comment. In the case of sodium iodide, on ac-

¹ RbI:	Schröder, <i>Loc. cit.</i>	3.023
	Setterberg, <i>Ibid.</i>	3.567
	Erdmann, <i>Arch. Pharm.</i> , 232, 25 (1894).....	...	3.447
	Buchanan, <i>Loc. cit.</i>	24.3°	3.428
	Baxter and Brink, <i>Ibid.</i>	25°/4°	3.438
² CsCl:	Setterberg, <i>Ibid.</i>	3.992
	Richards and Archibald, <i>Proc. Am. Acad.</i> , 38, 453 (1903).....	20°/4°	3.972
	Buchanan, <i>Loc. cit.</i>	23.1°	3.982
³ CsBr:	Setterberg, <i>Ibid.</i>	4.463
	Richards and Archibald, <i>Ibid.</i>	20°/4°	4.380
	Buchanan, <i>Ibid.</i>	21.4°	4.455
⁴ CsI:	Setterberg, <i>Ibid.</i>	4.537
	Beketoff, <i>Bull. St. Petersb.</i> , 34, 197 (1905).....	...	4.523
	Buchanan, <i>Loc. cit.</i>	22.8°	4.508
	Baxter and Brink, <i>Ibid.</i>	25°/4°	4.510

count of the hygroscopicity of the anhydrous salt, the value for the density is less reliable than that found earlier by Baxter and Brink, who investigated salt which could not have come into contact with moist air. The value for the coefficient of expansion of this salt found in this research is more accurate than the values of the density. Using the value 0.000136 for the coefficient of expansion of sodium iodide and the value 3.665, found by Baxter and Brink for the density at 25°, the density at 50° becomes 3.653 and that at 0° is 3.677. The first two sets of values with potassium chloride were obtained with powdered salt which had previously been fused, the third set with crystals from aqueous solution which had been carefully dried, powdered, and dried as in the experiments with fused salt. Apparently the salt crystallized from aqueous solution has a slightly lower density. Rubidium iodide is here found to have a density considerably higher than the value found by Baxter and Brink. But the latter did not use material of unquestionable purity, and since the material used here was found to be very pure, the later value is to be preferred.

The coefficients of expansion are of the order of magnitude to be expected from the rather meager data previously obtained with anhydrous salts.¹ It can be seen that with any one salt the coefficient of expansion is lower at high temperatures than at low temperatures. In general, chlorides show smallest and iodides largest coefficients, and, while this is by no means always the case, coefficients are usually higher with increasing density and increasing compressibility.

The results of the foregoing research may be summed up in the following brief tables:

TABLE II.

The densities of the following salts are found to be:

	70.19°.	50.04°.	25.00°.	0.00°.
NaCl.....	2.153	2.156	2.161	2.168
NaBr.....	..	3.194	3.203	3.213
NaI.....	..	3.653 ²	3.665 ²	3.677 ²
KCl.....	1.978	1.981	1.987	1.992
KBr.....	..	2.740	2.749	2.756
KI.....	..	3.114	3.123	3.133
RbCl.....	..	2.792	2.798	2.806
RbBr.....	..	3.340	3.349	3.358
RbI.....	..	3.542	3.550	3.560
CsCl.....	3.952	3.961	3.974	3.988
CsBr.....	..	4.418	4.433	4.449
CsI.....	..	4.493	4.509	4.525

¹ K₂SO₄..... 0.0108 20°

Rb₂SO₄..... 0.0106 20° Landolt-Börnstein-Roth, *Tabellen*, 1912.

Cs₂SO₄..... 0.0105 20°

KNO₃..... 0.0191 20°

² Computed from the coefficient of expansion.

³ Baxter and Brink, *Loc. cit.*

TABLE III.

The cubical coefficients of expansion of the following salts are found to be:

	70-50°.	50-25°.	25-0°.
NaCl ¹	0.000074	0.000106	0.000125
NaBr.....	0.000119	0.000122
NaI.....	0.000136	0.000135
KCl ¹	0.000083	0.000117	0.000084
KBr ¹	0.000125	0.000112
KI ¹	0.000114	0.000122
RbCl.....	0.000082	0.000111
RbBr.....	0.000101	0.000113
RbI.....	0.000092	0.000112
CsCl.....	0.000109	0.000136	0.000137
CaBr.....	0.000137	0.000141
CaI.....	0.000146	0.000146

We are greatly indebted to the Carnegie Institution for very generous assistance in pursuing this investigation.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE DENSITIES AND CUBICAL COEFFICIENTS OF EXPANSION OF CERTAIN SUBSTANCES: As_2O_3 , PbCl_2 , PbBr_2 , NdCl_3 .

BY GREGORY PAUL BAXTER AND CHARLES FRANCIS HAWKINS.

Received November 15, 1915.

Investigations now in progress or just completed in this laboratory have required an exact knowledge of the specific gravities of the compounds mentioned in the title, in order that, in weighing these substances, corrections for the buoyant effect of the air might be made with certainty. Since the experimental work was performed with considerable care, and since incidentally the cubical coefficients of expansion of three of these substances were found, the results are presented here by themselves.

The specific gravities were found by displacement of toluene in pycnometers, while the coefficients of expansion were computed from the specific gravities at different temperatures.

Two forms of pycnometer were employed. One was devised by Baxter and Hines² for experiments with very hygroscopic substances, and is a modification of a pycnometer described by T. W. Richards for the determination of the specific gravity of solids. A weighing bottle was provided with two glass stoppers, one of which was of ordinary shape and was used

¹ Fizeau, *Compt. rend.*, 64, 314 (1867), found the linear coefficients of expansion of sodium chloride and of potassium chloride, bromide, and iodide to have at 40° the values 0.000040, 0.000038, 0.000042 and 0.000043, whence the cubical coefficients of expansion may be calculated to be 0.000120, 0.000114, 0.000126 and 0.000129.

² *Am. Chem. J.*, 31, 220 (1904).

during the weighing of the substance. Into the other were sealed two capillary tubes which served to fill the bottle with liquid. The weighing bottle and the pycnometer stopper were both made of thick glass in order to avoid distortion when the stopper was inserted.

The salt, contained in a platinum boat, was fused in a suitable atmosphere in a quartz tube which was connected by a ground joint with a bottling apparatus, by means of which the boat, after being heated, could be transferred to the weighing bottle without exposure to moist air.¹ The salt was heated until fusion had taken place and the fused salt was limpid and free from bubbles of gas. The boat was then allowed to cool, and after the fusion atmosphere had been displaced by nitrogen, and the nitrogen in turn by dry air, the boat was transferred to the weighing bottle and weighed.

After the weighing of the salt, the ordinary stopper was removed, enough toluene to cover the boat and salt was quickly poured into the bottle, and the pycnometer stopper, which had been weighed with a small quantity of sirupy phosphoric acid to make the joint tight, was inserted. In order to expel the air contained in the crevices of the salt the pycnometer was placed in a vacuum desiccator, which was then exhausted, and the toluene was allowed to boil gently for some time with frequent jarring. By means of the capillary tubes the bottle was completely filled with toluene, and, while the pycnometer was immersed as far as possible in a water thermostat at 25°, the toluene was adjusted to a mark etched upon one of the capillaries. The weight of the system was then determined, after the pycnometer had been wiped with a clean, slightly moist cloth and had been allowed to stand in the balance case for a few moments. Prolonged standing in the balance case produced no difference in weight. After a second adjustment of the toluene the system was again weighed, and sometimes a third setting was made. In every case the weights agreed within a few tenths of a milligram. The weight of the pycnometer containing the empty boat and filled with toluene was determined several times. From the average of these weights, the weight of the salt, and the weight of the system including the salt and filled with toluene, the specific gravity of the salt was calculated.

The pycnometer described above was not adapted to determinations below the temperature of the room, since it had no reservoir for expansion of the liquid. For work both at 0° and at 50° a graduated flask was used as described by Baxter and Wallace.² The neck of this flask had been constricted at one point to 2.5 mm., which secured an accuracy in setting of about 0.3 mg. of toluene. Since comparatively large amounts

¹ Richards and Parker, *Proc. Am. Acad.*, 32, 59 (1897).

² See preceding paper, *THIS JOURNAL*, 38, 259 (1916).

of solid were used with this pycnometer the accuracy of setting was ample for the purpose.

Both pycnometers were "set" in water thermostats, the temperatures of which were controlled within a few hundredths of a degree, by means of toluene regulators at 25° and 50°, and by means of a large amount of washed cracked ice at 0°. The method of heating the water of the thermostat by passing a current through the water between carbon electrodes, as recently proposed by Derby,¹ was found to serve very satisfactorily at 50°. The thermometers were carefully corrected by comparison with a standard thermometer.

One specimen of arsenic trioxide was the commercial article, which was in the form of a fine powder. Another specimen was resublimed in a current of nitrogen by Mr. G. L. Wendt. As both were exposed to the air for some time before use they were probably octahedral.

Lead chloride was precipitated from lead nitrate and after washing was recrystallized from water. Finally it was fused in a current of hydrochloric acid gas. The fused material was irregular in appearance, and as the determinations with the bottle pycnometer gave discordant results, further experiments were made in the flask pycnometer with salt which, after fusion in hydrochloric acid, had been finely ground in an agate mortar. Since the latter experiments gave concordant results, which were somewhat higher than those obtained with the bottle pycnometer, it seemed highly probable that the latter were vitiated by pockets of gas in the fused material.

Lead bromide was precipitated from pure lead nitrate with hydrobromic acid, and was crystallized from concentrated hydrobromic acid solution before fusion in nitrogen containing hydrobromic acid gas. Determinations made with both pycnometers were concordant, although the material used in the flask pycnometer was finely powdered.

Praseodymium chloride was purified by Mr. O. J. Stewart and fused in a current of hydrochloric acid gas. Because of the hygroscopic nature of the anhydrous salt, determinations were made with the bottle pycnometer only, at 25°.

Toluene was dried over metallic sodium and distilled, the first and last portions being discarded. The specific gravities of the two specimens of the same sample of toluene were determined in both pycnometers.

Weights were carefully standardized to tenths of a milligram. Vacuum corrections are applied as follows:

Toluene.....	+0.00125
As ₂ O ₃	+0.000166
PbCl ₂	+0.000059
PbBr ₂	+0.000035
NdCl ₃	+0.000154

¹ THIS JOURNAL, 35, 1767 (1913).

The assumption is made that an "apparent" gram of water occupies, 1.01313 cc. at 50°, 1.00400 cc. at 25°, 1.00119 cc. at 0°.

Specific Gravity and Coefficient of Expansion of Toluene.

Sample of toluene.	Temp.	Pycnometer.	Apparent wt. of H ₂ O content. Grams.	Volume. cc.	Wt. of toluene in vac. Grams.	Spec. grav.	Coefficient of expansion. ¹
I....	50°	Flask	24.3408	24.6605	20.6566	0.83764	(50-25°)
	25°	Flask	24.5442	24.6424	21.2232	0.86125	0.000111
	0°	Flask	24.5991	24.6283	21.7806	0.88437	(25-0°)
	25°	Bottle	11.2314	11.2763	9.7123	0.86130	0.000106
II....	50°	Flask	24.3408	24.6605	20.6561	0.83762
	25°	Flask	24.5454	24.6436	21.2238	0.86123	(50-25°)
	0°	Flask	24.5991	24.6283	21.7797	0.88433	0.000111
	25°	Bottle	11.2332	11.2781	9.7130	0.86123	(25-0°)
							0.000106

 Specific Gravity and Cubical Coefficient of Expansion of As₂O₃.²

Temp.	Pycnometer.	Wt. of As ₂ O ₃ in vacuum. Grams.	Wt. toluene displaced in vac. Grams.	Sp. gr. toluene.	Sp. gr. As ₂ O ₃ .	Cubical coeff. expansion of As ₂ O ₃ .
25°	Flask	17.5146	3.9013	0.86125	3.867	(50-25°)
50°	Flask	27.0732	5.8881	0.83764	3.851	0.00012
25°	Flask	27.0732	6.0350	0.86125	3.863	(25-0°)
0°	Flask	27.0732	6.1802	0.88437	3.874	0.00011

¹ The values given in this column agree almost exactly with those found for Samples II and III in the preceding paper.

² Previous determinations:

- | | |
|-------------------|--|
| 3.695 octahedral | } Guibourt, <i>Bers. Jahresb.</i> , 7, 128 (1828). |
| 3.739 amorphous | |
| 3.729 at 17.2° | Herapath, <i>Phil. Mag.</i> , 64, 321 (1829). |
| 3.703 | } Karsten, <i>Schweig. J.</i> , 65, 394 (1832). |
| 3.720 | |
| 3.884 Filhol, | <i>Ann. chim. phys.</i> , [3] 21, 415 (1847). |
| 3.798 Taylor, | <i>Gmelin's Handb.</i> , 1, 69 (1848). |
| 3.698 vitreous, | LeRoyer and Dumas, <i>Ibid.</i> |
| 3.85 native, | Claudet, <i>Jahresb.</i> , 21, 230 (1868). |
| 3.80 regular | } Rammelsberg, "Handb. d. Krystallog. u. phys. Chem.," |
| 4.00 rhombic | |
| | Abt. I, 1881. |
| 3.682 amorphous | } Winkler, <i>J. prakt. Chem.</i> , 31, 247 (1884). |
| 3.643 crystalline | |
| 3.70 Leonhard, | Clarke's "Const. of Nature," Pt. I, 48 (1888). |

Specific Gravity and Cubical Coefficient of Expansion of PbCl_2 .¹

Temp.	Pycnometer.	Wt. PbCl_2 in vac. Grams.	Wt. toluene dis- placed in vac. Grams.	Sp. gr. toluene.	Sp. gr. PbCl_2 .	Cub. coeff. expansion of PbCl_2 .
25°	Bottle	5.3723	0.7960	0.86125	5.813
25°	Bottle	9.0828	1.3511	0.86125	5.790
25°	Bottle	7.3128	1.0922	0.86125	5.766
25°	Bottle	5.5365	0.8118	0.86125	5.874
25°	Bottle	6.6033	0.9791	0.86125	5.808
25°	Bottle	6.5749	0.9757	0.86125	5.804
25°	Bottle	6.2361	0.9222	0.86125	5.824
50°	Flask	32.0341	4.5697	0.83762	5.872
50°	Flask	25.7836	3.6774	0.83762	5.873
Av., 5.872						(50-25°)
25°	Flask	32.0341	4.6890	0.86123	5.884	0.00009
25°	Flask	25.7836	3.7727	0.86123	5.886
Av., 5.885						(25-0°)
0°	Flask	32.0341	4.8044	0.88433	5.896	0.00009
0°	Flask	25.7836	3.8642	0.88433	5.901
Av., 5.899						

Specific Gravity and Cubical Coefficient of Expansion of PbBr_2 .²

Temp.	Pycnometer.	Wt. PbBr_2 in vac. Grams.	Wt. toluene dis- placed in vac. Grams.	Sp. gr. toluene.	Sp. gr. PbBr_2 .	Cub. coeff. expansion of PbBr_2 .
25°	Bottle	7.3694	0.9531	0.86125	6.659
25°	Bottle	6.9347	0.8984	0.86125	6.648
						(50-25°)
50°	Flask	23.1459	2.9171	0.83762	6.644	0.00009
25°	Flask	23.1459	2.9926	0.86123	6.659	(25-0°)
0°	Flask	23.1459	3.0651	0.88433	6.676	0.00010

Specific Gravity of PrCl_3 .

Temp.	Pycnometer.	Wt. PrCl_3 in vac. Grams.	Wt. toluene dis- placed in vac. Gram.	Sp. gr. toluene.	Sp. gr. PrCl_3 .
25°	Bottle	3.6689	0.7862	0.8612	4.019
25°	Bottle	4.5130	0.9669	0.8612	4.020
Av., 4.020 ³					

¹ Previous determinations:

- 5.29 Munro, Clarke's "Constants of Nature," Pt. I, 24 (1888).
 5.238 native, Dana, "Mineralogy," 1892.
 5.802 unfused }
 5.682 fused } Karsten, *Schweig. J.*, 65, 394 (1832).
 5.802 cryst., Schabus, *Jahresb.*, 3, 322 (1850).
 5.78 Schiff, Clarke's "Constants of Nature," *Loc. cit.*
 5.805 15°, Stolba, *J. prakt. Chem.*, 97, 503 (1866).
 5.88 Brugelmann, *Ber. d. deutsch chem. Gesell.*, 17, 2359 (1891).

² Previous determinations:

- 6.630 Karsten, *Schweig. J.*, 65, 394 (1832).
 6.611 17.5°, Kremers, *Jahresb.*, 5, 397 (1852).
 6.572 19.2° precipitated, Keck, Clarke's "Constants of Nature," Pt. I, 32 (1888).

³ Matignon found the value 4.017 at 18°, *Compt. rend.*, 140, 340 (1905).

SUMMARY.

Substance.	Temperature.	Specific gravity.	Cub. coeff. of expansion.
As_2O_3	50°	3.851	(50-25°)
	25°	3.865	0.00012 (25-0°)
	0°	3.874	0.00011
PbCl_2	50°	5.872	(50-25°)
	25°	5.885	0.00009 (25-0°)
	0°	5.899	0.00009
PbBr_2	50°	6.644	(50-25°)
	25°	5.669	0.00009 (25-0°)
	0°	6.676	0.00010
PrCl_3	25°	4.020	

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, THE UNIVERSITY OF CHICAGO.]

STUDIES IN CONDUCTIVITY. III. FURTHER STUDIES ON THE BEHAVIOR OF THE ALKALI METAL FORMATES IN (ANHYDROUS) FORMIC ACID.

BY H. I. SCHLESINGER AND CLYDE COLEMAN.¹

Received December 4, 1915.

The work herein reported is a continuation of that of Schlesinger and Martin² on the conductivity of formic acid solutions of formates. It was shown by them that the formates of sodium, potassium, ammonium and phenyl ammonium obey *the law of chemical equilibrium* over a fairly large range of concentration *even though these salts are highly ionized*, provided that the degree of ionization is calculated without reference to the viscosity of the solutions. When a viscosity correction was made it was found that the agreement between the law and the experimental data disappeared. It was pointed out, however, that the viscosity data might have been somewhat inaccurate because a small viscometer of the Ostwald type was used. Hence it seemed necessary to repeat the viscosity determinations under more favorable experimental conditions. Furthermore, since the simple inverse proportionality between viscosity and conductivity, as predicted by Stokes' law does not usually fit experimental data on conductivity, information on the possible relation was sought by

¹ The work presented in this article constitutes the basis of a dissertation submitted by Clyde Coleman to the faculty of the University of Chicago in part fulfillment of the requirements for the degree of Doctor of Philosophy.

² THIS JOURNAL, 36, 1589 (1914). We shall use the abbreviation S. and M. hereafter in referring to this paper.

obtaining conductivity and viscosity data at two temperatures. Investigation of these points fully confirmed the work of S. and M. Strong electrolytes, however, do not in general obey the law of chemical equilibrium. Hence it was desired to extend the measurements to as many uni-univalent salts as possible and we, therefore, chose the as yet uninvestigated formates of the alkali metals. In this way we have obtained the ionization constants of a series of salts within the same chemical group and the values of these constants show some interesting relationships. We shall, however, present first the new experimental data in their entirety and leave the discussion of the results to a brief summary.

In most of the details the methods of S. and M. were followed without change. The formic acid was prepared according to their method and was of the same quality as reported by them.¹ The solutions were made up and the conductivities and densities measured as described by them. In place of the small Ostwald viscometer which they used, and which gave too short a period of transpiration to assure agreement with Poiseuille's law and accurate time measurement, we employed a quartz viscometer, made according to the directions of Washburn and Williams.² The formates were prepared from the carbonates by treatment with formic acid. The sodium formate was part of the same sample as that used in the previous work. Lithium formate was recrystallized from the anhydrous acid, the resulting product heated for about a day at 125° to drive off most of the acid and then recrystallized from alcohol. The rubidium carbonate from which the formate was made contained a small amount of potassium as revealed by the spectroscope. The formate on recrystallization from the acid retained the latter so tenaciously that it was necessary to neutralize the residual acid with the carbonate before recrystallization from alcohol. The final sample did not show the potassium lines; as the rubidium and potassium red lines are so close together it is possible that a trace of potassium remained in the salt, but it must have been very small. The procedure for the preparation of caesium formate is like that for the rubidium salt except that ether must be added to reprecipitate the salt from the alcohol solution. The original caesium carbonate contained sodium. Here likewise there appeared to be only a trace, if any, of the impurity left after the recrystallizations. All of the salts were analyzed by conversion into the sulfate and found pure within the limits of the analytical method. Rubidium and caesium formates are exceedingly hygroscopic. They were, therefore, always kept in a glass stoppered weighing tube, one end of which was drawn out so as to fit the neck of the volumetric flask. This permitted the transfer and weighing of the material, prelim-

¹ The conductivity of the acid at 25° averaged about 6.4×10^{-3} and at 18° about 5.6×10^{-3} reciprocal ohms.

² THIS JOURNAL, 35, 737 (1913).

inary to making the solutions, with a minimum exposure to moisture.

Table I gives the data for the conductivity of sodium formate at 18°. In Col. 1 is given the concentration c in gram mols per liter of solution; in Col. 2 the specific conductivity (χ) in reciprocal ohms; in Col. 3, the specific conductivity (χ_s) corrected for the conductivity of the solvent; in Col. 4 the equivalent conductivity (λ_s) calculated from the corrected specific conductivity; in Col. 5 the degree of ionization (α), the necessary λ_0 being found by plotting $C\lambda_s/1000$ against $100/\lambda_s$;¹ in Col. 6 the ionization constant K as given by the equation $\alpha^2c/1 - \alpha = K$; and in Col. 7 the percentage error in the measured conductivity which would account for the deviations of the individual values of K from the average value. This percentage error is given because relatively large deviations in the constant may be due to very small errors in the conductivity, which is the measured quantity most liable to error. It will be seen that this error does not exceed in any case 0.20%.

TABLE I.—THE CONDUCTIVITY OF SODIUM FORMATE SOLUTION AT 18°
In Anhydrous Formic Acid.

C.	χ .	χ_s .	λ_s .	α .	K.	% error.
0	57.57
0.05869	0.003206	0.003152	53.71	0.933	0.760	0.16
0.06438	0.003495	0.003441	53.31	0.926	0.746	0.00
0.07724	0.004115	0.004059	52.55	0.913	0.738	0.10
0.08320	0.004418	0.004364	52.33	0.909	0.759	0.15
0.09323	0.004886	0.004832	51.83	0.900	0.757	0.10
0.09739	0.005074	0.005018	51.52	0.895	0.741	0.05
0.1111	0.005696	0.005642	50.78	0.882	0.732	0.19
0.1158	0.005909	0.005855	50.55	0.878	0.732	0.20
0.1310	0.006611	0.006555	50.02	0.869	0.755	0.15
0.1365	0.006828	0.006774	49.63	0.862	0.734	0.17
0.1569	0.007711	0.007656	48.78	0.847	0.738	0.15
0.1660	0.008108	0.008054	48.52	0.843	0.750	0.06
0.1808	0.008722	0.008666	47.93	0.832	0.748	0.05
0.1878	0.009014	0.008960	47.71	0.829	0.752	0.14
0.2238	0.01043	0.01037	46.35	0.805	0.744	0.04
0.2794	0.01253	0.01248	44.66	0.776	0.750	0.10
0.2832	0.01267	0.01261	44.55	0.774	0.749	0.13
0.2997	0.01330	0.01324	43.99	0.764	0.741	0.16
0.3258	0.01417	0.01412	43.34	0.753	0.746	0.00
0.3453	0.01480	0.01474	42.70	0.742	[0.735]	..

Av., 0.746

Table II gives the viscosity data obtained with the quartz viscometer.² In Col. 1 are presented the concentrations (c) in gram mols per liter of solution; in Col. 2 the relative viscosity, $\text{rel } \eta_{25^\circ}$, of the solution at 25°;

¹ See Kraus and Bray, *THIS JOURNAL*, 35, 1324 (1913); also S. and M., p. 1596.

² The simple formula, $\eta_2 = \eta_1 t_2 d_1$, can be used with this instrument and the viscosities were calculated by its means from the time of transpiration and the densities.

in Col. 4 and 6 the densities (d_{18°) and the relative viscosities, $\text{rel } \eta_{18^\circ}$, respectively of the solutions at 18° . The viscosity data obtained with the quartz viscometer and those obtained with the small Ostwald instrument have been compared with one another by means of the interpolation formula which was found by S. and M. to reproduce their values.¹ These calculated values are found in Col. 3 and are seen to be in excellent agreement with those obtained in the more reliable Washburn viscometer. Hence we may conclude that all of the viscosity data of S. and M. have the same degree of reliability as those for the sodium formate solutions because for all of them the same instrument was used and about the same range of time of transpiration obtained. It is to be noted that the relative viscosities at 25° are based on the viscosity of the pure acid at this temperature, while those at 18° are based on the viscosity of the acid at 18° .² Finally it is possible to reproduce accurately the relative viscosity of the solutions at 18° by the method of interpolation used for the 25° data. This consists of choosing values for A corresponding to the concentration c and substituting them in the formula

$$\eta_{18^\circ} = 1 + Ac.$$

The values, A, for the different concentrations are given in Col. 5.

TABLE II.—RELATIVE VISCOSITY OF SODIUM FORMATE SOLUTIONS IN ANHYDROUS FORMIC ACID AT 25° AND 18° , AND DENSITIES AT 18° .

C.	rel η_{25°	rel η_{25° calc.	d_{18°	A $_{18^\circ}$	rel η_{18°
0	1.0000	1.0000	1.0000
0.05741	1.0408	1.041
0.06191	1.2254	0.756	1.0468
0.08267	1.2262	0.747	1.0618
0.1263	1.0876	1.086
0.1283	1.2275	0.735	1.0943
0.1962	1.1359	1.136
0.2107	1.2304	0.732	1.1543
0.2629	1.1834	1.181
0.3027	1.2331	0.732	1.2216
0.3708	1.2649	1.264
0.4925	1.2400	0.764	1.3763
0.5617	1.4103	1.409
0.5642	1.2421	0.771	1.4352

The densities at 18° can be reproduced very accurately by the formula

$$d = 1.2233^3 + 0.0335c.$$

¹ *Loc. cit.*

² The values of the viscosity of the pure acid at the two temperatures are given on p. 279.

³ It is to be noted, however, that the density of formic at 18° was found to be 1.2224 in several actual determinations. This figure was used in calculating the viscosities, as the difference is not within the error of the viscosity measurements. The analogous formula for rubidium formate solutions also contains the value 1.2233.

In Tables III and IV are given the conductivity data, together with the calculations for the equilibrium constants for lithium formate solutions at 25° and 18°, respectively. The various columns correspond entirely to those in Table I. It will be seen that the agreement with the equilibrium

TABLE III.—THE CONDUCTIVITY OF LITHIUM FORMATE SOLUTIONS AT 25°
In Anhydrous Formic Acid.

C.	x.	x_a .	λ_a .	α .	K.	% error.
0.00000	64.62
0.05748	0.003446	0.003379	58.79	0.9101	0.530	0.00
0.06920	0.004062	0.003995	57.74	0.8938	0.521	0.12
0.07777	0.004517	0.004450	57.22	0.8856	0.533	0.06
0.08100	0.004693	0.004626	56.98	0.8821	0.535	0.09
0.08619	0.004932	0.004865	56.43	0.8736	0.520	0.20
0.1102	0.006113	0.006047	54.85	0.8491	0.527	0.12
0.1218	0.006658	0.006591	54.11	0.8377	0.527	0.13
0.1365	0.007338	0.007270	53.30	0.8252	0.532	0.05
0.1550	0.008172	0.008105	52.30	0.8096	0.534	0.10
0.1785	0.009178	0.009111	51.07	0.7906	0.533	0.09
0.1955	0.009901	0.009834	50.31	0.7791	0.537	0.25
0.2078	0.01039	0.010326	49.70	0.7694	0.533	0.10
0.2331	0.01139	0.01132	48.57	0.7518	0.531	0.04
0.2622	0.01249	0.01242	47.37	0.7333	0.529	0.05
0.2833	0.01327	0.01321	46.62	0.7217	0.530	0.00
0.3056	0.01408	0.01401	45.85	0.7098	0.530	0.03
0.3081	0.01412	0.01405	45.62	0.7062	0.523	
0.3374	0.01513	0.01507	44.66	0.6914	0.522	
0.3605	0.01588	0.01581	43.86	0.6789	0.517	
0.3869	0.01671	0.01664	43.01	0.6658	0.513	
0.4272	0.01792	0.01786	41.81	0.6472	0.507	
0.4545	0.01874	0.01868	41.10	0.6363	0.506	
0.4938	0.01978	0.01972	39.93	0.6182	0.494	

TABLE IV.—THE CONDUCTIVITY OF LITHIUM FORMATE SOLUTIONS AT 18°
In Anhydrous Formic Acid.

C.	x.	x_a .	λ_a .	α .	K.	% error.
0	56.79
0.07305	0.003748	0.003691	50.53	0.8898	0.525	0.16
0.08728	0.004377	0.004320	49.51	0.8718	0.517	0.05
0.1257	0.005983	0.005925	47.15	0.8303	0.511	0.14
0.1678	0.007621	0.007567	45.09	0.7940	0.513	0.06
0.1690	0.007665	0.007608	45.02	0.7929	0.513	0.12
0.2018	0.008855	0.008799	43.60	0.7678	0.512	0.12
0.2054	0.008997	0.008939	43.50	0.7660	0.515	0.01
0.2216	0.009569	0.009510	42.92	0.7558	0.518	0.10
0.2531	0.01063	0.01057	41.75	0.7353	0.517	0.05
0.2642	0.01098	0.01092	41.36	0.7283	0.516	0.01
0.3045	0.01225	0.01219	40.05	0.7052	0.514	0.08
0.3598	0.01383	0.01377	38.27	0.6739	0.500	
0.4178	0.01540	0.01535	36.74	0.6470	0.495	
0.4501	0.01623	0.01617	36.04	0.6347	0.496	
0.4834	0.01698	0.01690	35.01	0.6130	0.469	

law at both temperatures is excellent; in only one experiment does the maximum experimental error corresponding to the deviation from the average value amount to more than 0.20%, and in most of them the error is only about one-half of this. Systematic deviation from the equilibrium law seems to begin at a concentration of about 0.3 molar, from which point, as the concentration increases, the value of the "constant" falls steadily.¹

In Table V are given the relative viscosity and the density data for lithium formate solutions at 25° and 18°. The meaning of the data in the various columns will need no further description. The terms relative viscosity are used in this table as in all others in the sense described in the discussion of Table II.

TABLE V.—RELATIVE VISCOSITY AND DENSITY OF LITHIUM FORMATE SOLUTIONS IN FORMIC ACID AT 18° AND 25°.

C.	d_{25}°	d_{18}°	rel η_{25}°	rel η_{18}°
0	1.2142	1.2224	1.0000	1.0000
0.08513	..	1.2242	..	1.0393
0.08583	1.2174	..	1.0566 ¹	..
0.08729	1.2164
0.1292	..	1.2255	..	1.0884
0.1347	1.2170	..	1.0885	..
0.1810	..	1.2264	..	1.1202
0.2039	1.2181	..	1.1330	..
0.2605	1.2190	..	1.1711	..
0.2703	..	1.2284	..	1.1861
0.3441	..	1.2301	..	1.2343
0.3446	1.2275 ²	..
0.4064	1.2223	..	1.2690	..
0.4335	..	1.2319	..	1.2914
0.4669	1.2240	..	1.3117	..

The densities of the solutions at 25° are accurately reproduced by the formula $d = 1.2142 + 0.021c$; at 18°, by the formula $d = 1.2224 + 0.0222c$.

As was pointed out by S. and M. the viscosities are not a linear function of the concentration, the constant A in the formula $\eta = 1 + Ac$ usually showing a minimum. The variation in A for the data at 25° is very small, however, in the case of lithium formate solutions, so that they can be reproduced fairly well by the formula $\text{rel } \eta_{25}^{\circ} = 1 + 0.66c$ while at 18° the formula $\text{rel } \eta_{18}^{\circ} = 1 + 0.695c$ gives merely a rough interpolation. The minimum, which is reached at a concentration about 0.18 molar, in the A value for the last equation is 0.68, which is sufficient to introduce an error greater than the experimental one.

¹ See S. and M., *Loc. cit.*, p. 1599.

² The viscosity of this solution was calculated from the density obtained by the formula.

In Table VI and VII are given the conductivity data for rubidium formate solutions at 25° and 18°, respectively. It will be seen that agreement with the equilibrium law is again excellent; in only one of the determinations is there an error greater than 0.2%. Systematic deviation from the law begins apparently at a concentration somewhat greater than 0.3 molar.

TABLE VI.—CONDUCTIVITY OF RUBIDIUM FORMATE SOLUTIONS IN FORMIC ACID AT 25°.

C.	x.	x_a	λ_a	α	K.	% error.
0	69.88
0.04964	0.003390	0.003322	66.92	0.9579	1.082	0.00
0.06852	0.004581	0.004517	66.86	0.9434	1.078	0.03
0.08026	0.005302	0.005238	65.27	0.9341	1.063	0.12
0.1088	0.007025	0.006961	64.05	0.9167	1.096	0.08
0.1489	0.009334	0.009272	62.29	0.8910	1.084	0.01
0.1742	0.01075	0.01069	61.33	0.8776	1.096	0.08
0.1990	0.01200	0.01194	60.30	0.8626	1.072	0.09
0.2438	0.01437	0.01431	58.70	0.8400	1.075	0.08
0.2779	0.01610	0.01603	57.70	0.8257	1.087	0.03
0.3096	0.01762	0.01755	56.69	0.8112	1.079	0.02
0.3477	0.01943	0.01937	55.69	0.7970	1.088	0.04
0.3877	0.02117	0.02110	54.44	0.7790	1.065	..
0.3924	0.02131	0.02125	54.23	0.7760	1.055	..
0.4237	0.02274	0.02268	53.53	0.7661	1.063	..

TABLE VII.—THE CONDUCTIVITY OF RUBIDIUM FORMATE SOLUTIONS IN FORMIC ACID AT 18°.

C.	x.	x_a	λ_a	α	K.	% error.
0	61.35
0.07128	0.004146	0.004094	57.37	0.935	0.964	0.17
0.1066	0.005994	0.005942	55.74	0.908	0.961	0.22
0.1583	0.008580	0.008524	53.82	0.877	0.995	0.05
0.1685	0.009071	0.009015	53.51	0.872	1.000	0.16
0.2200	0.01143	0.01138	51.73	0.843	0.999	0.10
0.2685	0.01358	0.01352	50.35	0.821	1.008	0.30
0.3210	0.01572	0.01566	48.80	0.796	0.994	0.05

In order to be able to make the calculation discussed in the footnote on p. 280, the densities of the rubidium formate solutions were determined to an accuracy of about 0.2% by the method already mentioned. The data for the individual experiments need not be given as the following formulas reproduce them sufficiently closely. At 25°

$$d = 1.2142 + 0.085c$$

and at 18°

$$d = 1.2233 + 0.080c.$$

In Table VIII are given the conductivity data for caesium formate solutions at 25°. Here again deviation from the equilibrium law is very small—in most cases far below 0.2%. Systematic deviation seems to begin at about 0.38 molar.

TABLE VIII.—CONDUCTIVITY OF CAESIUM FORMATE SOLUTIONS IN ANHYDROUS FORMIC ACID AT 25°.

C.	x.	x_g .	λ_g .	α .	K.	% error.
0	64.96
0.03057	0.002001	0.001938	63.39	0.9756	1.193	0.03
0.05543	0.003515	0.003454	62.29	0.9586	1.230	0.16
0.07919	0.004899	0.004836	61.07	0.9399	1.164	0.03
0.1019	0.006185	0.006121	60.09	0.9249	1.160	0.10
0.1419	0.008374	0.008311	58.57	0.9013	1.169	0.04
0.2008	0.01142	0.01136	56.55	0.8704	1.174	0.01
0.2577	0.01421	0.01415	54.90	0.8449	1.186	0.01
0.2961	0.01601	0.01595	53.84	0.8286	1.186	0.01
0.3449	0.01816	0.01810	52.47	0.8076	1.169	0.15
0.3893	0.01996	0.01989	51.10	0.7864	1.159	..

Summary.

1. The solutions of the highly ionized formates of lithium, rubidium and caesium in (anhydrous) formic acid are found to obey the law of chemical equilibrium over a fairly large range of concentration when the degree of dissociation is calculated from the conductivity data without correction for the changing viscosity of the solutions. For the formates of sodium, lithium and rubidium this has been established at the two temperatures, 25° and 18°. Table IX gives a list of the formates thus far investigated from this point of view, and summarizes briefly the numerical values of a number of the important constants. In the table, K means the equilibrium constants; the other headings need no further explanation.

TABLE IX.—TABLE OF CONSTANTS.¹

Substance.	K_{25}° .	K_{18}° .	λ_{25}° .	λ_{18}° .	$\lambda_{25}^{\circ}/\lambda_{18}^{\circ}$.
Lithium formate.....	0.530	0.515	64.6	56.8	1.138
Phenyl ammonium formate.....	0.798*	...	64.7*
Sodium formate.....	0.815*	0.746	65.4*	57.6	1.135
Potassium formate.....	1.019*	...	68.9*
Rubidium formate.....	1.082	0.989	69.9	61.3	1.139
Caesium formate.....	1.181	...	65.0
Ammonium formate.....	1.230*	...	69.9*

Av., 1.137

There are a number of regularities which may be pointed out very briefly.

(1) The value of the constant increases with the atomic weight of the alkali metal ion² and consequently also with the electrolytic solution tension of the metal. In the same way, the value of the conductivity at infinite dilution increases with the atomic weight, but in this series there is a striking exception in the case of caesium. Furthermore it will be seen

¹ Data marked * are taken from the work of S. and M.

² Leaving out of consideration, of course, the ammonium and the phenyl ammonium ions.

that the constant at 18° is, in each case where the data are at hand, less than that at 25° indicating that the process of ionization in these solutions is accompanied by absorption of heat.¹ If we use these data for a rough calculation of the heat of dissociation by means of the formula

$$\frac{d \ln K}{dt} = \frac{Q}{RT^2},$$

integrated on the assumption that the heat of reaction is constant over this small range of temperature we obtain about 700, 2180 and 2200 cal. for the heat of dissociation of lithium, sodium and rubidium formates, respectively. In aqueous solutions it is believed that the degree of electrolytic dissociation of the strong electrolytes usually decreases with rise of temperature, whereas in the cases here described the reverse is true.

(2) We have repeated the work of S. and M. on the viscosity of sodium formate at 25°, using a Washburn quartz viscometer, and have found that the new data correspond practically exactly with the older ones. Hence we may have the same degree of confidence in all of the older data on the viscosity of formate solutions as has already been explained. Furthermore, while all of the conductivity data thus far at hand agree with the demands of the equilibrium law if the degree of dissociation is calculated from the equation $\alpha = \lambda/\lambda_0$, none of them show this agreement if the equation $\alpha = \eta \lambda/\lambda_0$ is used,² where η is the relative viscosity of the solutions. Since it has been frequently suggested that a more suitable equation for calculating the degree of dissociation is $\alpha = (\eta)^2 \lambda/\lambda_0$ we have compared the viscosities of the solvent and the conductivities at infinite dilution at two temperatures (18° and 25°) for three of the formates in order to get some indication of the value of " p ." It will be seen from Col. 5 of Table IX that the ratio of the conductivities at infinite dilution (λ_0) at the two temperatures is practically the same for the three substances for which we have the necessary data; the difference between them, about 0.35%, is probably within the range of experimental error when it is considered that each λ_0 value is obtained by extrapolation. The viscosity of formic acid was found by us to be 0.01865 at 18°, while at 25° it was 0.01605. The ratio of viscosities at the two temperatures is, therefore, 1.16, while the average of the inverse of the corresponding ratio of λ_0 values is 1.14,

¹ By means of the density data given in this paper and in that of S. and M., it is possible to calculate the concentrations of the solutions in terms of gram molecules per 1000 cc. of solvent instead of 1000 cc. of solution as herein given. From these new values for the concentrations new values for the equivalent conductivities and for the constants can be obtained. While these new constants differ somewhat from the others, their *relative* value is the same and the agreement with the equilibrium law is as good as when calculated the other way. Also of course the calculated values for Q are the same as those given herein.

² The data resulting from these calculations have not been presented in this paper because they are just like those given by Schlesinger and Martin.

a difference of 1.8% which is far beyond the experimental error. The simple Stokes' law, therefore, is not applicable; an equation for α of the type mentioned above would have the form

$$\alpha = \frac{\lambda}{\lambda_0} (\eta)^{0.88}$$

if we assume for the present that the relationship between the conductivity and the viscosity, when the latter is changed by change in temperature, is the same as the (possible) relationship between conductivity and viscosity when the latter is changed by change in the concentration of the solutions. If α is calculated from this equation and substituted in the equation for the equilibrium law, no agreement is found with the demands of the latter.¹ Hence we believe that the conclusion of Schlesinger and Martin that in these solutions the true degree of dissociation is to be found from the conductivities without application of viscosity corrections has been corroborated, for we do not believe it possible that agreement as close as we have found between the equilibrium law and these conductivities could result from accidental cancelations of errors in the case of seven different substances, for some of them at two different temperatures.

The work on the behavior of formates and other salts in anhydrous formic acid as solvent is being continued along the lines already mentioned in previous papers. In addition, transference experiments are under way and the effect of the addition of non-ionized substances to the solvent is being investigated.

CHICAGO, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY.]

THE INTERACTION OF HYDROGEN AND CHLORINE UNDER THE INFLUENCE OF ALPHA PARTICLES.

By HUGH STOTT TAYLOR.

Received December 2, 1915.

In a recent communication to THIS JOURNAL,² the author recorded the results of certain investigations into the combination of hydrogen and chlorine under the influence of the energy obtained from radium emanation. By a study of the velocity with which the reaction proceeded the possible mechanism of the reaction was deduced and the conclusion was reached that the process was parallel in several important respects to that occurring in the photochemical combination of the two substances. The work which had been carried out in the laboratories of the Technische Hochschule, Hanover, Germany, was interrupted by the abnormal situa-

¹ See footnote 2, p. 279.

² THIS JOURNAL, 37, 24 (1915).

tion which arose in Central Europe last year, and as a consequence the results obtained did not represent the final conclusions from the work in hand. Since publication, the additional material obtained has been worked through and has led to several modifications of the original communication which it is desired here briefly to record.

In a personal communication, Professor Max Bodenstein, under whose direction the work was carried out, has called the attention of the writer to an error which was made in the original calculations from the velocity data which, when considered alone, modified considerably the actual results obtained. Further, to the then available results there is now to be added one further series, confirmatory of the preceding experimental work and supplying a basis for the consideration of several other factors of interest in the investigation. Also, consideration has been given to another factor, the correction factor for the alpha particles not absorbed by the gas but reaching the walls of the containing vessel there to lose the charge. Finally, from the available data, a computation has been made as to the amount of reaction between the constituents which the energy of the alpha particles could effect. It is the purpose of the following to summarize these several points.

As to the error in the calculation of the results from the experimental data. Reference to the original communication (pages 29 and 32) shows that the gases were analyzed after absorption in potassium iodide by titration with standard thiosulfate solution and estimation of the hydrochloric acid with standard baryta solution. To ensure greater accuracy, the acid titer was made with a baryta solution exactly one-third the strength of the thiosulfate solution. In the tables, the titers were presented in equivalent units. The solutions used were actually $N/20$ and $N/60$, respectively. From these tables of titers the actual volumes of hydrogen, chlorine and hydrogen chloride, as well as their respective partial pressures, could be calculated. In the calculations previously made the sum of the three gases in the sample analyzed was set equal to $(2 \times \text{Thio titer} + \text{Baryta titer})$, on the assumption that Cl_2 was equal to H_2 , and that, therefore, for the hydrogen there must be reckoned the same amount as for the chlorine. Obviously this is an error, since it overlooks the fact that the thiosulfate solution is $N/20$ with regard to Cl_1 and not for Cl_2 , and that, therefore, the thio titration represents Cl_2 only when divided by two; then, to get the total for hydrogen and chlorine this has again to be multiplied by two. In other words, the thiosulfate titration as communicated in the original paper represents as it stands $\text{H}_2 + \text{Cl}_2$. The data previously obtained had, therefore, all to be subjected to the recalculation which the discovery of this error necessitated. Naturally in the earlier measurements of a series, in which the thiosulfate titration is large compared with the baryta, the divergence from the former values was con-

siderable. The more hydrochloric acid produced, however, the less the divergence became.

Series 1.											
t.	P.	Titr.		2HCl.		Cl.		Rmana- tion cor- rection.	G.	h. P/Rm. G.	
		Ch.	HCl.	a.	b.	a.	b.				
0	676.5	18.35	0.50	9.4	11.8	328.9	326.5	0.997	0.99	5.2	} 11.8
1	657.5	16.27	0.66	11.5	26.1	317.3	303.2	0.984	0.98	18.4	
2.75	638.7	16.50	1.36	25.4	45.7	294.0	273.7	0.965	0.98	12.1	
6.67	620.7	13.80	2.20	44.4	67.9	266.0	242.5	0.932	0.97	13.0	
11.67	602.8	12.45	3.30	65.9	117.3	235.5	184.1	0.873	0.96	13.5	
24.80	585.2	9.30	5.66	113.8	131.1	178.8	171.1	0.809	0.95	11.6	
31.50	569.7	8.85	6.87	127.7	157.7	157.2	127.2	0.743	0.95	9.8	
47.9	551.8	6.90	8.17	
General mean,										12.0	

Series 2.											
0	698.5	16.65	0.566	12.0	13.8	337.3	336.5	0.997	0.99	3.7	
1	678.7	18.00	0.706	13.4	21.5	326.0	317.9	0.989	0.99	17.5	
2	660.0	15.63	1.01	20.8	39.2	309.2	290.8	0.978	0.98	18.9	
4	640.7	15.70	1.973	38.1	53.3	281.5	266.3	0.963	0.98	18.8	
6	622.7	13.10	2.533	52.4	62.4	259.0	249.0	0.949	0.97	13.3	
8	577.2	12.80	3.066	57.9	107.4	230.7	181.2	0.910	0.95	17.5	
17.2	526.1	9.00	5.10	98.0	112.2	165.1	150.9	0.867	0.93	16.6	
20.75	435.9	8.13	5.783	93.0	...	125.0	...	0.846	
General mean,										17.1	

Series 3.											
0	697.5	19.15	0.466	8.3	15.6	340.5	333.4	0.993	0.99	7.4	} 10.3
2.1	678.8	17.10	0.80	15.2	26.5	324.2	312.9	0.978	0.99	13.2	
4	658.6	17.20	1.466	25.7	35.0	303.6	294.3	0.963	0.98	10.7	
6	640.2	13.60	1.617	34.0	80.4	286.1	239.7	0.921	0.98	12.6	
16.1	620.2	13.12	4.40	77.8	90.3	232.3	219.8	0.874	0.97	10.3	
20	602.8	12.20	5.017	87.8	101.6	213.6	199.4	0.845	0.96	10.0	
25.1	303.2	11.10	5.65	52.3	82.8	99.3	68.9	0.773	0.73	10.1	
43.5	294.4	3.80	4.50	
General mean,										10.6	

Series 4.											
0	858.0	15.76	7.66	144.6	154.0	284.4	275.0	0.997	1.00	(28.2)	
1	835.2	13.12	7.02	149.8	154.9	267.8	262.7	0.989	1.00	16.2	
2	807.2	14.18	7.99	149.6	154.8	254.0	248.8	0.978	1.00	17.0	
3	756.0	10.98	6.533	145.0	155.3	233.0	222.7	0.971	1.00	17.6	
5	733.2	12.00	8.00	150.6	158.9	216.0	207.7	0.956	1.00	15.0	
7	671.3	10.30	7.523	145.4	180.8	190.3	154.9	0.915	0.99	15.2	
17	652.7	7.20	8.04	175.8	181.1	150.4	145.3	0.874	0.98	13.7	
19	601.5	7.27	8.656	166.9	172.8	133.9	128.0	0.859	0.96	12.3	
21.6	585.4	5.96	7.693	168.2	176.3	124.5	118.4	0.841	0.95	15.9	
24.7	544.3	5.72	8.333	164.4	192.5	107.8	79.7	0.787	0.94	13.9	
41.5	528.0	4.33	9.99	186.6	193.2	77.4	70.8	0.720	0.93	15.0	
46.2	510.0	3.86	10.07	
General mean,										15.2	

Series 5.

t.	P.	2HCl.		Cl ₂ .		Emanation correction.	G.	h. P/Em. G.
		a.	b.	a.	b.			
0	873.1	126.8	216.9	325.4	235.3	0.946	1.00	19.7
15.0	800.0	198.7	214.1	217.7	200.3	0.883	1.00	21.5
18.1	778.0	208.3	220.5	194.7	182.5	0.863	1.00	18.3
21.3	725.0	205.4	213.7	170.1	161.7	0.844	1.00	14.7
24.0	706.3	208.2	250.5	157.7	115.4	0.789	0.99	18.1
39.7	685.0	243.0	256.0	112.8	99.8	0.725	0.99	17.8
46.2

General mean, 18.2

To the original material of the previous communication, recalculated in accordance with the above, there is now added a series (5) performed with the same emanation as that employed in Series 4 of the original work, with gas, however, which was obtained after regeneration of the hydrochloric acid solution from which the gases were prepared by electrolysis. The run of the figures obtained is in every way similar to those previously recorded. It will be shown, however, that the gases employed were considerably more reactive, due to replenishment of the hydrochloric acid used.

The correction for incomplete absorption of the alpha particles by the gas may now be considered. The range of the bulb employed was approximately 5.6 cm. in air. According to Rutherford¹ the range in hydrogen-chlorine-hydrochloric acid is greater than this. From the ionization curves there given, it is possible to effect a correction for the alpha particles which reach the outer glass walls. In this regard it must be observed that the range 5.6 cm. of the small bulb refers to the rays from Radium C alone and in this particular calculation for those radiations only which travel normally through the walls of the emanation bulb. The radiations from the emanation and from Radium A will all be absorbed in the gas. Also the alpha particles from Radium C passing transversely through the walls of the emanation bulb have a longer path in the glass and naturally, therefore, a shorter in the gas. It is possible, as was done by Lind,² to make an exact calculation of the alpha particles which so behave and to correct for them, but since the alpha particles whose activity is lost in the walls of the containing vessel forms but a small fraction of the total number emitted into the vessel, the correction employed has been taken as one-half of that correction which would be required were all the alpha particles from the Radium C to leave the emanation bulb normal to the bulb surface. In the preceding tables under G there is recorded the fraction of the alpha particles which are absorbed in the gas. The velocity

¹ "Radioactive Substances and their Transformations," p. 161, *et seq.*

² *Sitz. der k. Akad. Wiss. Wien.*, 70 (1911); *Wiener, Monatsh.*, 32, 295 (1912).

constant must be corrected, therefore, for this factor by dividing the constant obtained $\frac{(k_1 \times P)}{\text{Emanation correction}}$ by the corresponding amount tabulated under G.

Certain conclusions may be drawn from the data yielded by the calculations tabulated above with regard to the reactivity of the gases used in the several series of measurements. In the earlier paper it was observed that a rough test of the gases towards light showed that they were by no means comparable in reactivity with the gases employed by Bodenstein and Dux. It was suggested that the cause lay in the exhaustion of the hydrochloric acid from which the gases were generated. This conclusion is confirmed by the following reasoning: Series 2 and 3 were carried out with the same filling of emanation. Likewise also were Series 4 and 5 effected with one sample of the emanation. Expt. 3 was started 24.75 hours later than Expt. 2. The emanation should, therefore, be 0.831 times less active in the later experiment. Were the gases of equal reactivity in the two series the velocity constant in the third series should be equal to $17.1 \times 0.831 = 14.2$. Actually, however, the value obtained was 10.6. The gases were, therefore, considerably less reactive. On the other hand, the time elapsing between the beginning of Expts. 4 and 5 was such that the emanation possessed only 0.686 of its value at the outset of Expt. 4, when the later series was started. In the intervening time, however, the hydrochloric acid had been replenished and so a more reactive gas mixture would be expected. That this is so is evident from the fact that $(0.686 \times k_4) = (0.686 \times 15.2) = 10.4$. Actually a reaction constant 18.2 was found. The gases were therefore considerably better.

It is of interest also to make a computation of the amount of reaction which is brought about by the energy supplied to the gaseous system. The emanation for an experiment was collected for four days from 10 mg. of radium bromide or in other units 6 mg. of radium. This quantity of material would yield approximately 3 millicuries of emanation in the given time. Assuming that of this quantity, the half ultimately arrived in the emanation bulb (which practical experience led one to believe) and that of this amount two-thirds was radiated into the gas and the remaining third was absorbed in the mercury, it may be computed that 4×10^{13} ions were radiated per second into the gas. In the most favorable case, the beginning of Series 2, the data obtained from the titers reveal that 7×10^{16} molecules of chlorine are converted per second into hydrogen chloride. That is, approximately 4000 molecules undergo reaction for each pair of ions radiated into a gas, which as regards light sensitivity was considerably inferior to that employed by Bodenstein and Dux and from which was calculated a reactivity of 10^6 molecules

per quantum of light energy. The comparability of the two reactions in this regard is, therefore, in good measure established.

Between the researches here presented in their modified form and the photochemical investigations of the same chemical reaction by Bodenstein and Dux, a considerable degree of parallelism is quite evident. Any theory that aims to represent the facts of the one must evidently suggest, also, explanation of the other. The hypothesis originally put forward by Bodenstein to account for the kinetics of the photochemical reaction covers equally well the facts obtained from this radioactive study. It has, however, excited from many quarters a considerable amount of criticism, which has called for a reconsideration of the original theory. The conclusions to which such reconsideration has led will form the subject of another communication elsewhere by Professor Bodenstein, to whom is due in large part whatever material gain in knowledge the investigations herein recorded have yielded.

PRINCETON, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY.]

THE OXIDATION OF HYDRAZINE. VII.

THE ALLEGED ROLE OF NITROUS ACID IN THE FORMATION OF HYDRONITRIC ACID.¹

By A. W. BROWNE AND O. R. OVERMAN.

Received August 26, 1915.

In a series of investigations² conducted in this laboratory, the behavior of a number of oxidizing agents toward hydrazine in aqueous solution, and usually in the presence of sulfuric acid, has been studied. On the basis of the results obtained it was found possible to classify the oxidizing agents provisionally into three groups comprising those substances that oxidize hydrazine at the boiling temperature in the presence of sulfuric acid:

- (a) with formation of fairly large amounts of hydronitric acid and ammonia;
- (b) with formation of little or no hydronitric acid, but large amounts of ammonia;
- (c) with formation of little or no hydronitric acid and ammonia. Hy-

¹ This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by O. R. Overman in partial fulfilment of the requirements for the Degree of Doctor of Philosophy. The experimental work was completed in June, 1915.

A typewritten copy of the original thesis will be found in the files of the Cornell University Library.

² Browne, *THIS JOURNAL*, 27, 551-5 (1905); Browne and Shetterly, *Ibid.*, 29, 1305-12 (1907); 30, 53-63 (1908); 31, 221-37, 783-99 (1909); Hale and Redfield, 33, 1353-62 (1911); Hale and Nunez, 33, 1555-63 (1911).

drogen peroxide, potassium chlorate, and potassium persulfate were found to be typical of the first group; potassium permanganate, manganese dioxide, and hydrated ferric oxide of the second group; and potassium iodate, mercuric oxide, and mercuric chloride of the third group.

From the list of substances thus studied and classified, all of the oxidizing agents that contain nitrogen, such as, for example, nitrous acid,¹ or its salts,² and esters,³ nitrogen trichloride,⁴ and nitric acid⁵ have been excluded. It has been shown previously by other investigators that various substances of this sort react with hydrazine under proper conditions yielding hydronitric acid. The nitrogen coupling involved in the transformation of hydrazine into hydronitric acid by means of such reactions, has hitherto been explained on the assumption that a more or less direct condensation of the oxidizing agent with the hydrazine takes place, as a result of which the nitrogen of the oxidizing agent, in certain cases at least or under certain conditions in a given case, probably participates in the synthesis of the N₃ group. In view of the very high yields of hydronitric acid obtained by Thiele and by Stollé⁶ by the action of alkyl nitrites upon hydrazine hydrate in alcoholic solution, it is obvious that the nitrogen of the oxidizing agent in this case participates quantitatively in the synthesis of the N₃ group. In the opinion of the authors, however, there is much reason to doubt whether or not in aqueous solution nitrous acid behaves solely in this way. The presence of nitrous oxide and of ammonia⁷ among the products of the interaction of nitrous acid and hydrazine in aqueous solution seems to indicate that a considerable part, at least, of the nitrous acid may behave after the fashion of certain oxidizing agents containing no nitrogen.

It has long been the contention of the authors and their co-workers, that the formation of hydronitric acid and ammonia in fairly large amounts from hydrazine by the action, in sulfuric acid solution, of oxidizing agents of the first class containing no nitrogen is to be explained by the initial formation of intermediate condensation products such as "buzylene,"

HN:N.NH.NH₃, or "aminotriimide," NH₂.N $\begin{matrix} \nearrow \text{N.H} \\ \searrow \text{N.H} \end{matrix}$, which subsequently

¹ Curtius, *Ber.*, 26, 1263 (1893).

² Angeli, *Atti accad. Lincei*, [5] 2, I, 569 (1893); *Chem. Centr.*, 1893, II, 559; Dennstedt and Göhlich, *Chem.-Ztg.*, 21, 876 (1897); *Chem. Centr.*, 1897, II, 1093; De Girard and de Saporita, *Bull. soc. chim.*, [3] 31, 905-7 (1904). See also Rimini, *Atti accad. Lincei*, [5] 14, I, 386-92 (1905); *Chem. Centr.*, 1905, I, 1546; E. Francke, *Ber.*, 38, 4102 (1905).

³ Thiele, *Ber.*, 41, 2681-3, 2806-11 (1908); Stollé, *Ibid.*, 41, 2811-13 (1908).

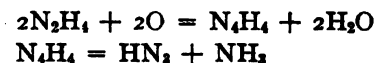
⁴ Tanatar, *Ibid.*, 32, 1399 (1899).

⁵ Sabanejeff and Dengin, *Z. anorg. Chem.*, 20, 21 (1899).

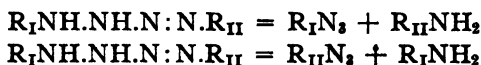
⁶ *Loc. cit.*

⁷ Francke, *Loc. cit.* See also THIS JOURNAL, 31, 783-99 (1909), p. 792, footnote 6.

decompose with formation of hydronitric acid and ammonia. The two stages of the reaction may be expressed by the following equations:



In support of this hypothesis may be cited the following facts: Diazobenzonimide and aniline may be obtained¹ by the oxidation of phenylhydrazine under certain conditions. Similar products are obtainable² by the decomposition of certain buzylenes in accordance with the equations:



Diazobenzonimide may be formed by the oxidation of phenylhydrazine³ with hydrogen peroxide.⁴

From a consideration of the analogy between hydroxylamine and hydrazine in their behavior toward oxidizing agents, A. Angeli⁵ has independently formulated an explanation of the formation of hydronitric acid as an oxidation product of hydrazine which is essentially similar to that just presented. In the opinion of Angeli the oxidation of hydroxylamine results in the formation of the unstable intermediate product "nitroxyl" which polymerizes to hyponitrous acid. This decomposes, yielding nitrous oxide and water. The entire process may be considered to take place in accordance with the following scheme:



In the case of hydrazine it is the opinion of Angeli that "diimide" is formed during the first stage of the reaction and at once polymerizes to form "tetrazone," which then decomposes, yielding hydronitric acid and ammonia. The progress of the reaction may be indicated as follows:



¹ E. Fischer, *Ber.*, 10, 1336 (1877).

² Curtius, *Ibid.*, 29, 759-83 (1896), p. 781. See also Wohl and Schiff, *Ibid.*, 33, 2741-58 (1900).

³ Wurster, *Ibid.*, 20, 2631-3 (1887).

⁴ From the fact that ammonia, as well as hydronitric acid, is obtained as a product of the oxidation of hydrazine with hydrogen peroxide it would seem very probable that not only diazobenzonimide but also aniline should be formed by the action of hydrogen peroxide upon phenylhydrazine.

⁵ *Atti accad. Lincei*, [5] 19, II, 94-101 (1910), p. 99. This article was not published until about one year after the appearance of the fourth article in the present series of investigations on the oxidation of hydrazine (*THIS JOURNAL*, 31, 783-99 (1909)), in which a detailed discussion of the theory here reviewed was presented. Inasmuch as no reference was made in the article of Angeli to the theory advanced by Browne and Shetterly, it is to be assumed that his conclusions were reached independently.

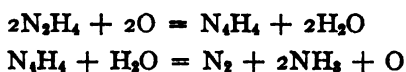
From this brief statement it will be at once recognized that the theory stated by Angeli is identical with that previously advanced by Browne and Shetterly, in that the formation of hydronitric acid and ammonia by the oxidation of hydrazine is explained on the assumption that intermediate condensation products of the nature of higher hydronitrogens are formed. One point of difference, however, lies in the fact that Angeli believes this intermediate product to be "tetrazone," while Browne and Shetterly have, for the reasons cited above, assumed it to be "buzylene" (or perhaps "aminotriimide"). This would seem to be justified by the fact that the derivatives of "tetrazone" yield on decomposition nitrogen and the derivatives of ammonia, while the derivatives of "buzylene" yield on decomposition the derivatives of both hydronitric acid and ammonia.

A second point of difference between the two statements of the theory lies in the assumption of Angeli that the product of the first stage of the reaction necessarily is "diimide." The authors are more inclined to believe with Browne and Shetterly that the initial product might take either the form $H_2N:N:$ or $HN:N'H$, according as two hydrogen atoms joined to the same or to different nitrogen atoms were first removed. Polymerization of two of the unsymmetrical residues would obviously yield "tetrazone," while polymerization of two of the symmetrical residues would be expected to yield "tetrimide." The formation of "aminotriimide" would take place by the union of one symmetrical with one unsymmetrical residue. The symmetrical residues might, of course, spontaneously take the form of "diimide" but it is difficult to see how two of these "diimide" molecules could polymerize to form "tetrazone" as assumed by Angeli.

The final stage of the reaction as the result of which ammonia and hydronitric acid are obtained from the intermediate condensation product, may simply consist in an intramolecular rearrangement of this product with formation of the empirically isomeric compound,¹ ammonium trinitride, which at once in acid solution yields an ammonium salt and free hydronitric acid.

¹ There is some reason to suppose that isomeric or perhaps tautomeric forms of ammonium trinitride may be capable of existence. In the course of an investigation completed in this laboratory some months ago, but still unpublished, Mr. F. Friedrichs discovered that ammonium trinitride forms three ammonates with the respective formulas $NH_4N_3.NH_3$, $NH_4N_3.2NH_3$, and $NH_4N_3.4NH_3$. It was found that while either the monammonate or the diammonate could be readily obtained under proper conditions, neither one could be directly prepared from the other by addition or removal of ammonia; or in other words, that no inversion point at which the diammonate was transformed into the monammonate could be located although the inversion of each of the compounds into anammonous ammonium trinitride and saturated solution was readily observable. These facts may possibly point toward the existence of at least two modifications of ammonium trinitride. Efforts to separate the two forms

In explanation of the behavior of oxidizing agents of the second class, such as potassium permanganate, manganese dioxide, and ferric oxide toward hydrazine in sulfuric acid solution, it has been assumed by the authors that varying amounts of some such intermediate condensation product as "tetrazone," $\text{H}_2\text{N}:\text{N}:\text{N}:\text{NH}_2$, are formed and are subsequently decomposed, yielding nitrogen and ammonia in accordance, perhaps, with the equations:



The reactions expressed by these equations may be regarded as strictly analogous with the formation of the tetrazones¹ by the oxidation with mercuric oxide of the unsymmetrical secondary hydrazines and with their decomposition in acid solution.²

Oxidizing agents of the third class, such as potassium iodate, mercuric oxide, and mercuric chloride, which ordinarily do not yield appreciable amounts of either hydronitric acid or ammonia, in all probability do not yield intermediate condensation products of the type presumably formed by the action of oxidizing agents of the first and second classes. The residues obtained as the initial product of the oxidation probably undergo complete oxidation to nitrogen and water before they have had time to polymerize, or in any event even if polymerization should be effected the more complex molecules must themselves be completely oxidized before they have had time to decompose into hydronitric acid and ammonia.

In a recent article, the theory of intermediate condensation products, reviewed in the preceding paragraphs has been adversely criticized by Sommer,³ who has presented an alternative hypothesis which, in his opinion, is less complicated and is in closer accord with the facts.

From the viewpoint of this hypothesis the oxidation of hydrazine by means of oxidizing agents such as hydrogen peroxide and potassium persulfate, which yield fairly large amounts of hydronitric acid and ammonia, may be considered to proceed in the following stages: (1) formation of ammonia as the initial oxidation product of hydrazine, (2) oxidation of the ammonia with formation of nitrous acid, (3) interaction of the nitrous acid with the excess of unchanged hydrazine with formation of hydrazine nitrite, (4) decomposition of the hydrazine nitrite, which proceeds in two by fractional sublimation did not, however, meet with success. In this connection it is interesting to note that Mendeléeff (*Ber.*, 23, 3464-72 (1890)), predicted the transformation of ammonium trinitride into an isomeric form. Further experiments will be performed in this laboratory with a view to obtaining the isomers of ammonium trinitride.

¹ See, for example, E. Fischer, *Ann.*, 199, 281-332 (1879).

² Renouf, *Ber.*, 13, 2169-74 (1880).

³ *Z. anorg. Chem.*, 86, 71-87 (1914).

concurrent reactions, one of which yields nitrous oxide, ammonia and water and the other hydronitric acid and water.

The formation of ammonia from hydrazine can indeed be readily accomplished as pointed out by Sommer. It is possible to obtain ammonia, for example, (1) by catalytic decomposition¹ of hydrazine, (2) by reduction² of hydrazine, and (3) by oxidation of hydrazine. The formation of ammonia by the third of these methods, which alone is of particular importance in the present discussion, has been repeatedly observed in this laboratory as a result of numerous reactions between hydrazine and the various oxidizing agents studied. In fact, no instance of the formation of hydronitric acid as a product of the oxidation of hydrazine without the simultaneous formation of ammonia³ has yet been recorded in this laboratory.

The ease with which ammonia may be experimentally obtained from hydrazine by various methods, however, affords no assurance that the mechanism of the reactions involved is necessarily simple. While the mechanism of the formation of ammonia and nitrogen by catalysis (which could be regarded as analogous with the formation of water and oxygen by the catalytic decomposition of hydrogen peroxide) or by reduction of hydrazine may be relatively simple, that of the formation of ammonia, which is normally to be considered a reduction product of hydrazine, as an *oxidation* product of hydrazine may well be more complicated. The splitting apart of the nitrogen atoms in the hydrazine molecule by oxidation, in the face of their strong tendency to escape in the form of molecular nitrogen, presents, to the minds of the authors at least, very nearly if not quite as difficult a problem as does the nitrogen coupling involved in the formation of hydronitric acid under these conditions. The authors find it impossible, then, to agree with Sommer that "seine Bildung über das Tétrazon zu erklären, erscheint daher sehr gezwungen." On the basis of their present knowledge of the subject the authors are unable to formulate an explanation of the formation of ammonia more satisfactory than that involving (1) the splitting off of one molecule of this substance from an unstable intermediate condensation product containing a chain of four nitrogen atoms, such as "buzylene" or "amino-triimide" the remaining three atoms of which would in either case retain

¹ Tanatar, *Z. physik. Chem.*, 40, 475-80 (1902); 41, 37-42 (1902); A. Purgotti and L. Zanichelli, *Gazz. chim. ital.*, 34, I, 57-87 (1904).

² W. T. Cooke, *J. Chem. Soc.*, 19, 213 (1903).

³ In the earliest investigation of the interaction of hydrogen peroxide and hydrazine sulfate conducted in this laboratory (*THIS JOURNAL*, 27, 551-5 (1905)), no attempt was made to detect ammonia in the products of the reaction. Later work upon the same reaction, however, showed conclusively that hydrogen peroxide was no exception to the general rule, but that large amounts of ammonia were formed during its interaction with hydrazine sulfate. See *THIS JOURNAL*, 31, 221-237 (1909), p. 231.

one hydrogen forming hydronitric acid, or (2) the splitting off of two molecules of ammonia by hydrolysis from a molecule of "tetrazone," in which case the remaining nitrogen would appear in the form of molecular nitrogen.

In view of these considerations it would seem fair to conclude that, unless Sommer can suggest a new and simpler explanation of the formation of ammonia as an oxidation product of hydrazine, his adoption of this reaction as the first stage in the process of obtaining hydronitric acid by the oxidation of hydrazine would seem to complicate, rather than to simplify, the issue.

The formation of nitrous acid by oxidation of ammonia can be effected under proper conditions. The literature of the oxidation of ammonia is very extensive. Among the investigators that have given attention to the oxidation of ammonia in aqueous solution may be mentioned the following: Loew¹ found that blue hydrated copper oxide in strong ammonium hydroxide solution oxidizes the ammonia to nitrous acid. Traube and Biltz² electrolyzed a solution containing ammonia, sodium hydroxide, and copper hydroxide, and found that nitrites and nitrates were formed. Müller and Spitzer³ observed the formation of nitrites when a solution of ammonia and an alkali was electrolyzed in the presence of copper hydroxide or with an iron anode. When no alkali was present, however, a nitrite which had been added to the electrolyte was destroyed and large amounts of gaseous nitrogen were evolved. When an acid or neutral solution of ammonium sulfate was electrolyzed with a platinum anode, ammonium persulfate and hydrogen were formed. Kempf⁴ allowed a solution of ammonium persulfate in a dilute solution of silver sulfate in sulfuric acid to stand at room temperature. Nitric acid was formed. In the absence of silver salts this oxidation did not take place. Levi and Migliorini⁵ heated alkaline and neutral solutions of ammonium persulfate. Part of the ammonia was oxidized to nitric acid. Herschkowitsch⁶ obtained nitrous acid and nitric acid by the action of potassium permanganate upon a neutral or an alkaline solution of ammonium sulfate. Brochet and Boiteau⁷ electrolyzed an ammoniacal solution of ammonium carbonate and noted the formation of nitrates. Alexjew⁸ electrolyzed a solution of ammonium sulfate using an anode of lead peroxide. In acid solution nitrous oxide and in alkaline solution nitrogen was formed. Reitlinger⁹

¹ *J. prakt. Chem.*, [2] 18, 298 (1878).

² *Ber.*, 37, 3130 (1904).

³ *Ibid.*, 38, 778 (1905); *Z. Elektrochemie*, 11, 917 (1905).

⁴ *Ber.*, 38, 3966-71 (1905); see also *Ibid.*, 38, 3972-4 (1905).

⁵ *Gazz. chim. ital.*, [2] 38, 10 (1908); *C. A.*, 2, 2912 (1908).

⁶ *Z. physik. Chem.*, 65, 93 (1908).

⁷ *Bull. soc. chim. de France*, [4] 5, 667 (1909).

⁸ *Jour. Russ. Phys.-Chem.*, 41, 1155 (1909); *Chem. Zentr.*, 1910, I, 403.

⁹ *Z. Elektrochem.*, 20, 261 (1914).

obtained nitrous acid in a solution of ammonium hydroxide and sodium hydroxide by electrolytic oxidation. Scagliarini and Casali¹ observed anodic oxidation of ammonia in an acid medium in the presence of silver salts. Nitric acid but no nitrous acid was produced.

From the foregoing citations it will be seen that the formation of nitrous acid and even of nitric acid by the chemical or by the electrochemical oxidation of ammonia in neutral or alkaline solution has repeatedly been effected. Up to the present, however, no evidence of the formation of these substances by the oxidation of ammonia in acid solution has been found by the authors, with the exception of that furnished by the work of Kempf² and of Scagliarini and Casali,³ who obtained nitric (but no nitrous acid) by the oxidation of ammonia in acid solution *in the presence of silver salts*. In connection with his investigation of the oxidation of ammonia both in alkaline and in acid solution in the presence and in the absence of silver sulfate Kempf makes the following statement:

"Bei Abwesenheit eines Silbersalzes ist dagegen eine Persulfatlösung nicht im Stande, gebundenes Ammoniak in schwefelsaurer Lösung zu Salpetersäure zu oxidieren. Es kommt diese energische Oxydationswirkung, die der von den Salpeterbakterien ausgeübten ganz analog ist, also nur dem Silberperoxyd zu, nicht der Ueberschwefelsäure oder den aus ihr leicht entstehenden, anderen oxydierenden Agentien: dem Ozon, der Caro'schen Säure oder dem Wasserstoffsuperoxyd."

Among the conclusions drawn by Kempf as a result of his work are the following:

(1) "Alkalipersulfat oxydirt in schwefelsaurer Lösung bei Gegenwart von Silbersulfat Ammoniumsalze schon bei gewöhnlicher Temperatur nahezu quantitativ zu Salpetersäure, (2) Bei Abwesenheit von Silbersalzen tritt diese Oxydation nicht ein."

Two references to the literature of nitrous acid were made by Sommer in support of his contention that the oxidation of hydrazine under the conditions prevailing in the experiments of Browne and Shetterly yields nitrous acid as a product of the alleged second stage of the reaction. The first reference is to a report of the work of Weith and Weber,⁴ the entire text of which is as follows:

"Die HH. Verfasser haben dagegen constatirt, dass Wasserstoffsuperoxyd und Ammoniak mit einander reichlich salpetrige Säure gaben, wodurch die Entstehung der salpetrigen Säure in der Natur eine einfache Erklärung findet."

This meager statement, which contains no information whatever concerning the conditions under which the experiment was performed, as, for example, whether the ammonia used was in the gaseous form, or was in acid, neutral or alkaline solution, has apparently been accepted by Sommer as a corroboration of his theory. The second reference is to the work of Kempf² who has made an explicit statement, which has already been quoted above, to the effect that in the absence of a silver salt neither

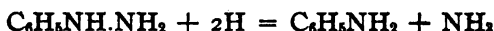
¹ *Atti accad. Lincei*, 21, II, 726 (1913); *C. A.*, 7, 1457 (1913).

² *Loc. cit.*

³ *Ber.*, 7, 1745 (1874).

persulfuric acid nor hydrogen peroxide oxidizes combined ammonia in sulfuric acid solution to nitric acid.

The reliability of the well-known Kjeldahl method¹ and its numerous modifications for the determination of nitrogen further attests the improbability of the formation of volatile nitrogen acids by the oxidation of ammonia in strongly acid solution. Powerful oxidizing agents are often used in connection with the determination of nitrogen by this method. Krüger² added a small excess of potassium dichromate to the mixture of the substance containing nitrogen with sulfuric acid in the digestion flask. The nitrogen determination was found to be accurate. In the determination of nitrogen in nitro and nitroso compounds³ the compound was first reduced by heating with stannous chloride to form the amido-derivatives and then the oxidation was carried on with potassium dichromate. Dakin⁴ used potassium persulfate to oxidize the organic matter rapidly and completely without loss of nitrogen. Milbauer⁵ determined nitrogen in phenylhydrazine and in various hydrazones and osazones. The substances were first reduced with nascent hydrogen from zinc dust and sulfuric acid. In the case of phenylhydrazine the reduction was expressed by the following equation:



Potassium persulfate was then added and the mixture was digested. The determination of nitrogen was accurate.

From the foregoing brief review of the literature it would appear that there is but little chance that nitrous acid could be formed under any ordinary conditions by the action of oxidizing agents upon ammonia in sulfuric acid solution. In order to ascertain positively, however, whether or not nitrous acid is formed under the particular conditions prevailing in the oxidation experiments of Browne and Shetterly, the authors have conducted an experimental investigation, the results of which will be discussed under the following headings: (1) materials used; (2) general procedure; (3) details of experiments; and (4) summary.

Materials Used.—The ammonium sulfate solution used in this investi-

¹ It has occurred to the authors that the formation of ammonia by the action of oxidizing agents in strong sulfuric acid solution upon various nitrogenous substances may be in a sense analogous to the formation of water in the presence of concentrated sulfuric acid from the hydrogen and oxygen contained in various organic substances. If we look upon the charring of such substances by the action of concentrated sulfuric acid as essentially a process of dehydration effected by the strong acid, it may not be unreasonable to regard the formation of ammonia as a process of deammonation effected by the sulfuric acid after the organic molecules have been in part broken up by the oxidizing agent.

² *Ber.*, 27, 609 (1894).

³ *Kruger, Ibid.*, 27, 1633 (1894).

⁴ *J. Soc. Chem. Ind.*, 21, 848 (1902).

⁵ *Z. anal. Chem.*, 42, 725 (1903).

gation contained 10.18 g. of the pure salt per liter and was thus of approximately equimolecular concentration with the 1% hydrazine sulfate solution employed in this laboratory in the oxidation of hydrazine. The various oxidizing agents were employed in the form and in the concentration used in these earlier experiments. The hydrogen peroxide solution was the ordinary 3% solution, 25 cc. of which, diluted with 50 cc. of distilled water, was used in each experiment. The potassium chlorate solution contained 9.423 g. per liter, while the solution of potassium permanganate contained 6.308 g. of this substance per liter. Potassium iodate was used in the form of a solution containing 16.458 g. per liter, while mercuric chloride was used in the form of its saturated solution of which 50 cc. were taken for each experiment. The insoluble, or difficultly soluble, oxidizing agents, including potassium persulfate, manganese dioxide, hydrated ferric oxide, and red mercuric oxide, were employed in the solid form.

The standard nitrite solution used in the experiments was of such concentration that 1 cc. contained 0.001 mg. of nitrogen in the form of potassium nitrite. The reagent employed in the detection of nitrous acid was a solution of α -naphthylamine and sulfanilic acid in 30% acetic acid.¹ The distilled water used throughout the entire investigation was shown by colorimetric tests made with this reagent to contain less than 0.005 part of nitrogen in the form of nitrous acid per million parts, that is, less than 0.005 mg. of nitrogen per liter.

General Procedure.—The apparatus employed in the experiments consisted of a liter distilling flask provided with a two-hole rubber stopper, through which passed the stem of a dropping funnel and a tube for the admission of a current of air. To the side arm of this flask was sealed a Reitmeier bulb, through which communication was established with a condenser. The receiver consisted of two 250 cc. Erlenmeyer flasks in series. The flask nearer to the condenser was connected to it by means of an adapter and contained at the outset 25 cc. of water, below the surface, of which dipped the lower end of the adapter. The second Erlenmeyer flask contained at the outset 10 cc. of water, into which dipped the end of the tube through which connection was established with the first flask.

In each of the experiments recorded in Tables I and II, 100 cc. of the ammonium sulfate solution were placed in the distilling flask, 50 cc. of concentrated sulfuric acid were added, and the resulting liquid was heated almost to the boiling point. The solution of the oxidizing agent was then added at the rate of about 40 drops per minute from a dropping funnel, the tip of which extended well below the surface of the liquid in the flask. In case the oxidizing agent was insoluble or difficultly soluble in water,

¹ E. M. Chamot and H. W. Redfield, "The Analysis of Water for Household and Municipal Purposes," pp. 23, 24, and 38 (1911) Taylor and Carpenter, Ithaca, New York.

it was introduced into the flask in solid form, and 100 cc. of the ammonium sulfate solution were poured in upon it. Then, after the mixture had been heated almost to the boiling point, the sulfuric acid was added drop by drop below the surface of the liquid. The solution in the flask was kept, in either case, at a temperature just below the boiling point during the whole time necessary to add the solution of the oxidizing agent or the sulfuric acid. The temperature was then raised to the boiling point and 100 to 150 cc. of liquid were distilled over. Throughout the entire experiment a slow current of air that had been purified by passing through Friederichs' gas washing bottles containing, respectively, concentrated sulfuric acid and concentrated potassium hydroxide solution was either drawn or forced through the apparatus. This served to keep the mixture in the flask well stirred and to sweep any volatile products of the reaction over into the receiver. After the distillation had been discontinued the liquids in the two receiving flasks were mixed and the resulting mixture was tested for nitrous acid.

In Table I are recorded certain particulars concerning the individual experiments performed with the various oxidizing agents in the attempt to obtain nitrous acid by the oxidation of ammonia. These experiments were carried out in such a way as to duplicate so far as possible in every respect the conditions that prevailed in the experiments of Browne and Shetterly on the oxidation of hydrazine. That the nitrous acid if formed even in mere traces would promptly be carried over into the receiver was demonstrated by means of a blank experiment in which a small sample of the standard nitrite solution was used.

TABLE I.

No. of expt.	Cc. H_2SO_4 .	Oxidizing agent.	Amount used.	No. of expt.	Cc. H_2SO_4 .	Oxidizing agent.	Amount used.
1	50	H_2O_2	25 cc. 3% with 50 cc. water	9	5	MnO_2	1.6 g.
2	50	H_2O_2	25 cc. 3% with 50 cc. water	10	5	MnO_2	1.6 g.
3	50	H_2O_2	25 cc. 3% with 50 cc. water	11	10	MnO_2	1.6 g.
4	10	KClO_3	67 cc.	12	25	Fe_2O_3 hydrated	2.0 g.
5	50	$\text{K}_2\text{S}_2\text{O}_8$	4.183 g.	13	25	Fe_2O_3 hydrated	5.0 g.
6	50	$\text{K}_2\text{S}_2\text{O}_8$	4.183 g.	14	10	KIO_3	50 cc.
7	50	KMnO_4	65 cc. with 325 cc. water	15	10	KIO_3	50 cc.
8	50	KMnO_4	65 cc. with 325 cc. water	16	25	HgO (red)	10.0 g.
				17	25	HgO (red)	10.0 g.
				18	25	HgCl_2 sat. soln.	50 cc.
				19	25	HgCl_2 sat. soln.	100 cc.

In no experiment were appreciable amounts of nitrous acid obtained. In several instances, it is true, traces of the acid were detected but never more than the almost infinitesimal amount present in the distilled water used. Some difficulty was experienced in the case of hydrogen peroxide and potassium chlorate, owing to the tendency for hydrogen peroxide and chlorine, respectively, to distil over into the receiver. Tests were

made in all cases for nitric acid by the ferrous sulfate method, but in no case was any indication of the presence of this acid obtained.

In a second series of experiments the solution in the distilling flask, after the distillation had taken place, was in each case made alkaline and the ammonia was distilled into standard sulfuric acid. The details of these experiments, in which three oxidizing agents of the first class have been used, are given in Table II.

TABLE II.

No. of expt.	Cc. H_2SO_4 .	Oxidizing agent.	Amount used.	Ammonia taken (g).	Ammonia found (g).	Percentage loss of NH_3 .
20	50	H_2O_2	25 cc. 3% 50 cc. water	0.2624	0.2607	0.64
21	50	H_2O_2	25 cc. 3% 50 cc. water	0.2624	0.2612	0.46
22	10	KClO_3	67 cc.	0.2624	0.2593	1.18
23	10	KClO_3	67 cc.	0.2624	0.2586	1.45
24	10	KClO_3	67 cc.	0.2624	0.2604	0.76
25	50	$\text{K}_2\text{S}_2\text{O}_8$	4.183 g.	0.2624	0.2615	0.34

From these experiments the conclusion may be drawn that ammonia is practically unaffected by treatment with hydrogen peroxide, potassium chlorate, and potassium persulfate in sulfuric acid solution. The largest amount of ammonia lost in any case (Expt. 23) amounted to 1.45%. Even if this had been quantitatively converted to nitrous or to nitric acid, the quantities of these substances thus formed would not, under the most favorable conditions, produce more than a small fraction of the hydronitric acid normally obtained by the oxidation of hydrazine with any one of the three oxidizing agents under consideration. Moreover, the possibility, or at any rate the probability, of the conversion of ammonia even in small amounts to nitrous or to nitric acid under the prevailing conditions, is virtually excluded by the experiments recorded in Table I.

It might possibly be contended that the influence of the unoxidized excess of hydrazine present in each experiment on the actual oxidation of hydrazine until the oxidation was nearly complete, might in some way favor the formation of nitrous acid by oxidation of ammonia; for example, by furnishing a means for the very rapid disposal of the nitrous acid as soon as it is formed. If this be, at all reasonable, and if the Sommer theory be correct, it is to be expected that the addition of ammonia to the reacting mixture should tend to increase the yield of hydronitric acid obtained, both by supplying material from which nitrous acid could be formed, and by sparing a corresponding amount of hydrazine for participation in the later stages of the reaction.

In case, however, the Sommer theory is not tenable, and the theory propounded by Browne and Shetterly is to be given credence, it would scarcely be expected that an increase in the yield of hydronitric acid should be obtained by the addition of ammonia to the reacting mixture. On the other hand, it is even possible that, by increasing the active mass of

ammonia, the decomposition of the intermediate condensation products (which yield, as stated above, either hydronitric acid and ammonia, or ammonia and nitrogen) might be retarded. This would result either in permitting their complete oxidation to nitrogen and water by the oxidizing agent, or even in facilitating their preservation in the unchanged condition in the residual liquid.

In order to ascertain the effect of adding ammonia to the reacting mixture of hydrazine sulfate and hydrogen peroxide in sulfuric acid solution three preliminary experiments have been performed. These experiments (the details of which are given in Table III) were performed under conditions exactly similar, except for the addition of ammonia, to those prevailing in the experiments described below (in Table IV) and in those described in the earlier articles of this series. The ammonia was added in the form used in the preceding series of experiments, namely, in the form of a solution of ammonium sulfate containing 10.18 g. per liter. In each case the volume of this solution taken was about one-half that of the hydrazine sulfate solution. This proportion was chosen in order that in the event of the quantitative oxidation of the ammonia to nitrous acid there would be formed one molecule of this acid for each molecule of hydrazine.

The procedure consisted in mixing the hydrazine sulfate and ammonium sulfate solutions with sulfuric acid in the usual distillation flask and then slowly introducing the hydrogen peroxide as before. The receiver contained, in place of pure water, 5 cc. of a 10% solution of silver nitrate, 2 cc. of a 10% solution of sodium acetate, and 35 cc. of distilled water. After the oxidizing agent had been added (at the rate of about 40 drops per minute) the solution was boiled until all of the hydronitric acid had been distilled into the receiver. The precipitated silver trinitride was then washed by decantation and was finally collected upon an asbestos filter in a tared Gooch crucible. The crucible with the precipitate was thoroughly dried in an evacuated desiccator over concentrated sulfuric acid and was weighed. The results were as follows:

TABLE III.

No. of expt.	Cc. H ₂ SO ₄ .	Cc. N ₂ H ₄ .H ₂ SO ₄ .	Cc. (NH ₄) ₂ SO ₄ .	H ₂ O ₂ .	AgN ₃ gram.
38	50	67	33	25 cc. 3% 50 cc. H ₂ O	0.0906
39	50	100	50	25 cc. 3% 50 cc. H ₂ O	0.1945
40	50	100	50	25 cc. 3% 50 cc. H ₂ O	0.1905

In Expt. 38 about one-third of the usual amount of hydrazine sulfate was replaced by an equimolecular quantity of ammonium sulfate. On the assumption that hydrazine might be quantitatively converted to ammonia and ammonia to nitrous acid, the yield of hydronitric acid obtainable under the conditions of Expt. 38 should be comparable with that from 100 cc. of the hydrazine solution in the absence of ammonia (See

Table IV). The actual yield obtained, however, was found to be less than half of this. Since it would scarcely be fair to draw conclusions from this experiment alone, Expts. 39 and 40, in each of which the full amount of hydrazine was used, were performed; but even in these cases the yields of silver trinitride were considerably lower than the average yield obtained when ammonium sulfate was absent. The average yield of silver trinitride obtained in the seven experiments on the oxidation of hydrazine by hydrogen peroxide in the absence of ammonia recorded in Table IV amounts to 0.2327 g. (max. 0.2468 g., min. 0.1891 g.). The results are entirely negative so far as any possible corroboration of the Sommer theory is concerned. The authors, however, do not venture to say, at the present stage of the work, that they afford distinct support to the theory of intermediate condensation products at present accepted in this laboratory. Further work on the influence of ammonium sulfate upon the yields of hydronitric acid and ammonia will be carried on, especially in the attempt to effect the isolation of the intermediate products by retarding their decomposition.¹

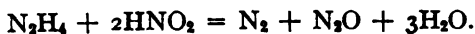
Since the failure to demonstrate the oxidation of ammonia to nitrous acid in sulfuric acid solution is very unfavorable, if not quite fatal, to the main contention of the Sommer theory, there is no need of discussing in detail in the present article the final stages of the reaction between hydrazine and oxidizing agents that contain no nitrogen, as they have been assumed to take place by Sommer. It is of course true that nitrous acid, if present, would oxidize hydrazine in acid solution under proper conditions to hydronitric acid. The interaction of these substances has been investigated during the past few years by a number of workers. In the opinion of de Girard and de Saporta² the reaction takes place as follows:



E. Francke³ calls attention to the formation of nitrous oxide and ammonia in accordance with the equation



while Dey and Sen⁴ believe that the reaction proceeds quantitatively in accordance with the equations



In the first of his "Studien über das Hydrazin und seine anorganischen Derivate"⁴ Sommer attributes the formation of hydronitric acid to the

¹ Various experiments of widely differing character are now in progress in this laboratory in connection with the search for the higher hydronitrogens.

² *Loc. cit.*

³ *Z. anorg. Chem.*, 71, 236-42 (1911); 74, 52-4 (1912).

⁴ *Ibid.*, 83, 119-137 (1913), p. 134.

action of undissociated nitrous acid upon hydrazine ions, perhaps in accordance with the equation



In his second article¹ he explains the simultaneous formation of hydronitric acid and ammonia as a result of the decomposition of hydrazine nitrite, which he believes to take place in two concurrent reactions, one of which yields nitrous oxide, ammonia, and water, and the other hydronitric acid and water.

The divergent conclusions reached by these investigators probably indicates that their experiments have been performed under different conditions. While not prepared, at the present writing, to formulate definitely their own views concerning the mechanism of the reaction, the authors will here simply reiterate the statement made sometime ago² to the effect that in aqueous solution one part of the nitrous acid may simply condense with the hydrazine to form hydronitric acid, while another part may decompose the hydrazine, after the manner of certain oxidizing agents containing no nitrogen, with formation of hydronitric acid and ammonia. This second process would, in the opinion of the authors, involve the formation of unstable intermediate condensation products, while the nitrous acid itself would probably undergo reduction to hyponitrous acid or nitrous oxide. Further work on this problem will be carried out in this laboratory in the near future with the especial object in view of comparing, over the widest possible range of conditions, the behavior of typical oxidizing agents containing no nitrogen with that of oxidizing agents containing nitrogen.

In order to obtain a comparison between the behavior of hydrogen peroxide and that of nitrous acid toward hydrazine under the usual conditions prevailing in the oxidation experiments, and especially from the viewpoint of the yields of hydronitric acid and ammonia, a preliminary series of experiments has been performed. The hydrogen peroxide used was a 3% solution which had been tested and found to be free from nitrites. The potassium nitrite solution contained 6.54 g. of the salt per liter and was thus of equimolecular concentration with the solution of hydrazine sulfate which contained 10.00 g. of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ per liter. The apparatus employed was similar to that used in the preceding series of experiments. The procedure was, briefly, as follows: in each case 100 cc. of hydrazine sulfate solution together with 50 cc. of concentrated sulfuric acid were introduced into the distilling flask. This mixture was heated to boiling and the oxidizing agent was introduced well below the surface of the liquid at the rate of about 40 drops per minute. In the one case 25 cc. of 3% hydrogen peroxide diluted with 50 cc. of distilled water,

¹ *Loc. cit.*

² THIS JOURNAL, 31, 783-99 (1909), p. 792, footnote 6.

and in the other 150 cc. of the solution of potassium nitrite were used, except in the case of Expts. 29 and 31, in which only 100 cc. were used. The reacting mixture was kept gently boiling throughout the addition of the oxidizing agent, and efficient stirring was effected by drawing a current of air through the liquid. The yields of hydronitric acid and ammonia were determined in the manner described above. In order to insure, so far as possible, the maintenance of similar conditions throughout the comparative study of the two reactions, the experiments in the two series, with the exception of Expts. 26 and 27 were carried out in parallel with the aid of two separate pieces of apparatus. The further details of the experiments are given in Table IV.

TABLE IV.

No. of expt.	Oxidizing agent.	AgN ₃ obtained (g.).	Yield HN ₃ (%).	NH ₃ obtained (g.).	Yield NH ₃ (%).
26	H ₂ O ₂	0.2366	40.96
27	H ₂ O ₂	0.2457	42.55
28	H ₂ O ₂	0.2448	42.50
29	KNO ₂	0.2026	35.15
30	H ₂ O ₂	0.2468	42.85	0.03466	52.97
31	KNO ₂	0.2592	45.00	0.01463	22.35
32	H ₂ O ₂	0.2318	40.25	0.03401	51.97
33	KNO ₂	0.3035	52.69	0.00898	13.73
34	H ₂ O ₂	0.1891	32.82	0.03579	54.69
35	KNO ₂	0.3117	54.12	0.01160	17.73
36	H ₂ O ₂	0.2340	40.37	0.03349	51.17
37	KNO ₂	0.2730	47.40	0.01039	15.88

In the foregoing table the yields of hydronitric acid and ammonia have been computed on the basis of the equation



The oxidation of hydrazine was complete in every case except in Expts. 29 and 31. Since the first six experiments were of a more or less preliminary character the results obtained in them have not been included in the average yields given below.

The average yield of silver trinitride obtained by the oxidation of hydrazine with hydrogen peroxide in Expts. 32, 34 and 36 is 0.2183 g., corresponding to 37.81% of hydronitric acid; the average yield of ammonia amounts to 0.03443 g., or 52.61%. The average yield of silver trinitride obtained by the interaction of potassium nitrite and hydrazine sulfate in Expts. 33, 35, and 37 is 0.2961 g., corresponding to 51.40% of hydronitric acid, while the average yield of ammonia is 0.01032 g., or 15.78%.

From these results it is apparent that the yields of hydronitric acid were distinctly larger and the yields of ammonia were distinctly smaller when nitrous acid was used than when hydrogen peroxide was taken as the oxidizing agent. This might well have been expected on the supposition that in the case of nitrous acid a part of the acid simply condenses

with the hydrazine to form hydronitric acid and water, the nitrogen of the acid participating in the synthesis of the N_2 group, while another part acts as an oxidizing agent with formation of intermediate condensation products which finally decompose with formation of both hydronitric acid and ammonia.

In connection with his discussion of the relative merits of the two theories, Sommer has taken occasion to state that the reference made by Browne and Shetterly to analogous reactions from the field of organic chemistry scarcely suffices to strengthen their theory. In the opinion of the authors, however, one of the most interesting chapters in the investigation of the hydronitrogens and their inorganic derivatives is that dealing with the analogy between the reactions of these substances and the reactions of their respective organic derivatives. It is, of course, well known that both hydrazine and hydronitric acid were known in the form of their organic derivatives long before they were isolated by Curtius, and that a knowledge of the properties and reactions of the organic derivatives played a vitally important part in the work of effecting their isolation. The authors are, moreover, of the opinion that future developments in the field of the inorganic hydronitrogens and particularly the discovery of new hydronitrogens will probably take place to a large extent along lines that have already been marked out by the organic chemist.

Summary.

In the investigation that has been described in the foregoing pages it has been shown:

(1) That no indication of the formation of appreciable quantities of nitrous acid or of nitric acid could be obtained by treatment of ammonium sulfate in sulfuric acid solution with oxidizing agents such as hydrogen peroxide, potassium chlorate, potassium persulfate, potassium permanganate, hydrated ferric oxide, potassium iodate, mercuric oxide, and mercuric chloride, under the conditions prevailing in the earlier experiments of Browne and Shetterly on the oxidation of hydrazine.

(2) That ammonium sulfate in a solution strongly acid with sulfuric acid is but slightly affected by prolonged treatment with such oxidizing agents as hydrogen peroxide, potassium chlorate, and potassium persulfate at the boiling temperature.

(3) That the addition of ammonium sulfate to a reacting mixture of hydrazine sulfate, sulfuric acid, and hydrogen peroxide does not increase, but rather serves to decrease, the yields of hydronitric acid obtained.

(4) That potassium nitrite oxidizes hydrazine sulfate in sulfuric acid solution with formation under comparable conditions of larger yields of hydronitric acid and of much smaller yields of ammonia than are obtained by the action of hydrogen peroxide upon hydrazine sulfate.

(5) That, in view of the experimental results obtained and of various

other considerations, the theory advanced by F. Sommer in explanation of the formation of hydronitric acid and of ammonia by oxidation of hydrazine by means of oxidizing agents that contain no nitrogen is, in all probability, to be regarded as untenable.

ITHACA, N. Y.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF NEODYMIUM.

[SECOND PAPER.]

BY GREGORY PAUL BAXTER, WILLIAM HENRY WHITCOMB, OLUS JESSE STEWART AND HAROLD CANNING CHAPIN.

Received November 11, 1915.

In an earlier investigation on the atomic weight of neodymium by Baxter and Chapin,¹ the material examined was purified first by crystallization of the double ammonium nitrate and then by crystallization of the nitrate from concentrated nitric acid. The first process was found particularly successful in eliminating samarium, the second in freeing the neodymium from praseodymium. The fractions in the final series were converted to chloride, which, after very careful dehydration, was analyzed by comparison with silver, with the result that the atomic weight of neodymium was found to be 144.27 ($A_g = 107.880$).

During the purification of the neodymium material as described above, attempts were made to free the neodymium from its companions by other methods. One of these was the fractional crystallization of the chloride. This crystallization proceeds less readily than that of either the double nitrate or nitrate, and after the process had been carried on for ten series of crystallizations little evidence of separation could be observed. At the same time another portion of the original material was converted to nitrate and fractionally crystallized from concentrated nitric acid. As the chief impurity, praseodymium, seemed to accumulate rapidly in the more soluble fractions, the portion which had been crystallized as chloride also was converted to nitrate and fractionally crystallized from nitric acid. Fractional crystallization of these two portions was carried on separately for some time, for 75 series with one portion, for 76 with the other, then the two portions were combined and further crystallized in the same way. Both the least soluble and the most soluble fractions frequently were rejected, the least soluble fraction to eliminate samarium, gadolinium, etc., the most soluble to remove praseodymium, cerium and lanthanum, for Demarçay² has shown that the separation occurs in this order. The least soluble fraction was thus forty times dis-

¹ *Proc. Amer. Acad.*, 46, 213 (1911); *THIS JOURNAL*, 33, 1; *Z. anorg. Chem.*, 70, 1.

² *Compt. rend.*, 122, 728 (1896); 130, 1021 (1900).

carded, the most soluble eighty-four times. After 158 series of crystallization in all had been carried out, the purity of the fractions of the last series, 17 in number, was investigated spectroscopically. As all of the fractions seemed to be fairly pure and the intermediate fractions very pure, it was decided, for the purpose of comparison with the material purified for the earlier investigation, to examine quantitatively the new material. Since at the outset only one and one-half kilograms of fairly pure double ammonium nitrate was used, the final fractions were not large, and, therefore, instead of analyzing each fraction separately, they were combined in pairs except that the three least soluble fractions, 2590, 2591 and 2592, were combined. The combinations actually analyzed were: 2590 + 2591 + 2592, 2593 + 2594, 2595 + 2596, 2597 + 2598, 2599 + 2600, 2601 + 2602, 2603 + 2604.

The purity of each of these combinations was carefully determined by photography of the visible and ultraviolet regions of the absorption spectrum with a Féry quartz spectrograph. The solutions were prepared by dissolving 2 g. portions of the ignited oxides in a slight excess of nitric acid and diluting the solution to a volume of about 10 cc. The absorbing layer was 10 cm. long. The less soluble fractions contained small amounts of samarium, and the more soluble ones praseodymium. In order to determine the proportions of these impurities, to a solution of a 2 g. portion of the oxide of Fraction 2605-6, which was free from samarium although it contained praseodymium, were added known amounts of a standard solution of pure samarium nitrate, the absorption spectrum of the solution being photographed after each addition of samarium.¹ By comparing photographs of the different fractions with those of the material containing known amounts of samarium, it was possible to estimate with considerable exactness the proportion of samarium² in the former. The percentage of praseodymium³ in the more soluble fractions was estimated in a similar fashion by comparing the photographs of the fractions analyzed with those of a solution of Fraction 2590-1-2, to which known amounts of praseodymium were added. The results of these comparisons are given below.

Fraction.	Samarium. %.	Fraction.	Praseodymium. %.
2590-2591-2592	0.6	2599-2600	0.00
2593-2594	0.4	2601-2602	0.05
2595-2596	0.2	2603-2604	0.1
2597-2598	0.1	2605-2606	0.2
2599-2600	0.0		

Since cerium and lanthanum nitrates are both more soluble in con-

¹ The samarium material was very kindly furnished by Professor C. James of New Hampshire College.

² Through the band λ 401.

³ Through the band λ 444.

centrated nitric acid than praseodymium nitrate, the quantities of these impurities remaining must have been very small indeed.

Although the proportions of impurity are small, yet because the atomic weights of both samarium and praseodymium are considerably different from that of neodymium it is not surprising that the extreme crystal fraction yielded a result somewhat higher than the average, and that the more soluble fractions apparently possessed an atomic weight slightly lower than the average. However, since the amounts of impurity were determined with some accuracy, corrections could be applied to the final result.

Preparation of Materials.

The Preparation of Neodymium Chloride.—In order to change the nitrate to chloride, essentially the same processes were employed as in the previous investigation. Neodymium oxalate was first precipitated by adding to the dilute solution of the nitrate a considerable excess of oxalic acid. The oxalate was collected upon a disk of filter paper in a porcelain Gooch crucible and after being dried was ignited to oxide in a platinum boat in an electrically heated porcelain tube, pains being taken to avoid heating the boat to a temperature at which platinum might vaporize into the contents.¹ The resulting oxide was dissolved in redistilled nitric acid in a quartz dish, and after the solution had been diluted, the oxalate was reprecipitated by means of a dilute solution of either recrystallized oxalic acid or recrystallized ammonium oxalate. The oxalate was washed, dried and ignited as before. Then it was dissolved in a quartz dish in hydrochloric acid which had been distilled through a quartz condenser, and the chloride was at least three times crystallized in quartz dishes by saturating the aqueous solution with hydrochloric acid gas at a low temperature. Centrifugal drainage of the crystals was always employed. The product was preserved in quartz in a desiccator containing fused sodium hydroxide.

Reagents.—Pure silver, water and reagents were prepared exactly as recently described in the account of similar work by Baxter and Stewart on praseodymium chloride.²

The Drying of Neodymium Chloride.—In the earlier work by Baxter and Chapin the attempt was made to prepare the salt for analysis by drying it carefully in a current of hydrochloric acid gas, and eventually fusing the salt. In the first experiments, the salt dried in this way invariably yielded a considerable amount of insoluble material, the exact nature of which was not discovered until later. Hence, the expedient was adopted of drying the salt for analysis as carefully as possible below the fusing temperature, and then determining the proportion of water

¹ See Baxter and Chapin, *THIS JOURNAL*, 33, 16 (1911).

² *THIS JOURNAL*, 37, 524 (1915).

retained. Ultimately it was found possible to obtain fused salt which would yield a perfectly clear solution, but the necessary information as to the proper treatment was obtained too late to be of service. It was partly because of the slight uncertainty involved in applying a correction for the residual water that the present investigation was undertaken. In the recent research by Baxter and Stewart upon praseodymium chloride a similar difficulty was met,¹ and in the latter research it was shown that the insoluble material is the oxychloride, and that its formation can be wholly or almost completely avoided by drying the salt as completely as possible previous to fusion, and then fusing the salt as rapidly as possible. No matter how carefully the preliminary drying is carried out, and no matter what precautions are taken in the drying of the hydrochloric acid gas in which the salt is fused, prolonged fusion invariably yields a very considerable proportion of insoluble matter, probably owing to a small amount of air contained in the hydrochloric acid gas. In these respects the neodymium chloride resembles the praseodymium salt exactly. A considerable amount of the insoluble neodymium compound was prepared by fusing some of the carefully dried chloride for an hour. The insoluble residue was collected and weighed, and its content of neodymium and chloride was determined. The results of these experiments indicate conclusively that the insoluble matter is the oxychloride. The following table contains the results of these experiments:

Weight of insoluble material.....	0.00775 g.
Weight of AgCl found.....	0.00602 g.
Weight of AgCl calculated from NdOCl.....	0.00568 g.
Weight of Nd ₂ O ₃ found.....	0.00685 g.
Weight of Nd ₂ O ₃ calculated from NdOCl.....	0.00666 g.

By following the same procedure in the drying of the neodymium chloride that was used in the drying of the praseodymium chloride, we were able to prepare salt which yielded immediately a clear solution. The details of this procedure are as follows: A platinum boat containing the powdered crystals of the hydrated salt was placed in a quartz tube forming part of a Richards "bottling apparatus." The bottling apparatus, which contained the weighing bottle in which the boat had initially been weighed, was connected with an apparatus for delivering dry hydrochloric acid gas, nitrogen and air. This apparatus is described in the paper on praseodymium chloride.² The boat was then gradually heated to a temperature slightly above 100°, but considerably lower than the transition temperature of the salt, 124°, until nearly all of the first five molecules of water of crystallization had been expelled by efflorescence. The temperature was then raised to 180° or thereabouts, where the sixth molecule

¹ THIS JOURNAL, 37, 527 (1915).

² *Ibid.*, 37, 526 (1915).

of water evaporates, and finally the salt was heated to about 350° for several hours. The aluminum block oven which had been used for producing uniform temperature up to this point was now replaced by an electrically heated sleeve, and the salt was brought to the fusing point, 785° ,¹ as quickly as possible. Then it was allowed to cool rapidly, and after the acid gas had been displaced by nitrogen and finally by air, the boat and contents were transferred to the weighing bottle without exposure to moisture and weighed. In a few cases a trace of insoluble salt was visible when the chloride was dissolved in water, but the proportions in these cases, judging from earlier experience, were less than 0.1 mg. By allowing the solution to stand for a day or two the basic salt dissolved completely. In Analyses 1, 2, 3, 5, 11, 13, 15, 16, 17, 18, 19, 21, 27, 29, 31 and 32 the solution of the chloride was clear at the outset.

Since the basic salt seems to form through the action of the air in the hydrochloric acid upon the fused salt more readily at higher than at lower temperatures, in three experiments the salt, after the usual careful preliminary drying, was heated almost, but not quite, to the fusing point for some time. In this way all but negligible amounts of water must have been expelled. In fact these analyses (Nos. 4, 7, 9, 20, 23 and 25) show a slightly greater percentage of chlorine, rather than smaller, than the specimens which were actually fused. In these cases also the salt yielded a perfectly clear solution.

The Method of Analysis.

The method of analysis was like that previously used with neodymium and praseodymium and other chlorides. The salt was dissolved in water and the solution was diluted to a volume of 1000–1500 cc. in a glass-stoppered precipitating flask. Pure metallic silver² equivalent to the chloride within a very few tenths of a milligram, was weighed out, dissolved in nitric acid and diluted to about the same volume. The silver solution was then added to the chloride solution in small portions with frequent agitation. After standing at room temperature for some time, the analysis was cooled to 0° , in order to reduce the solubility of silver chloride,³ and the clear solution was tested in a nephelometer for excess of chloride or silver. The estimated deficiency of either was added in the form of hundredth normal solution, and the solution was again thoroughly shaken, allowed to clarify and tested as before, and the process was repeated until exactly equivalent quantities of silver and chloride had been used.

In the analyses by Mr. Whitcomb, after the end point of the comparison had been reached, an excess of 0.05 g. of silver nitrate was added for each liter of solution and the analyses were allowed to stand some time longer

¹ Matignon, *Compt. rend.*, 133, 289 (1901); 140, 1340 (1905).

² The silver used had already been tested in the praseodymium work.

³ Richards and Willard, *THIS JOURNAL*, 32, 32 (1910).

at 0°. Then the silver chloride was washed several times with ice-cold silver nitrate solution containing 0.05 g. per liter and many times with ice-cold water, before being collected on a weighed platinum-sponge Gooch crucible. The chloride was dried in an electrically heated air bath at 190° for at least 18 hours and weighed. Residual moisture was determined by the loss in weight when the main bulk of the precipitate was fused in a porcelain crucible. The weight of silver chloride dissolved in one liter of the filtrate and silver nitrate washings was assumed to be 0.000004 g. per liter.¹ Chloride dissolved in the aqueous washings together with that obtained from the precipitating flask was estimated by nephelometric comparison with standards.

TABLE I.
The Atomic Weight of Neodymium.

$\text{NdCl}_3 : 3\text{Ag}$.

$\text{Ag} = 107.880$. $\text{Cl} = 35.457$.

Number of analysis.	Analyst.	Fraction.	Weight of NdCl_3 in vacuum. Grams.	Weight of Ag in vacuum. Grams.	Weight of Ag added or subtracted. Gram.	Corrected weight of Ag in vacuum. Grams.	Ratio $\text{NdCl}_3:3\text{Ag}$.	Atomic weight of Nd.
1	Whitcomb	2590-1-2	3.34038	4.31322	-0.00035	4.31287	0.774514	144.293
2	Stewart	2590-1-2	4.03869	5.21540	-0.00095	5.21445	0.774519	144.294
Average,							0.774517	144.294
3	Whitcomb	2593-4	4.48251	5.78795	-0.00035	5.78760	0.774503	144.289
4 ²	Whitcomb	2593-4	3.75204	4.84483	-0.00025	4.84458	0.774482	144.282
5	Stewart	2593-4	6.00909	7.75942	-0.00050	7.75892	0.774475	144.280
Average,							0.774487	144.284
6	Whitcomb	2595-6	4.96466	6.41065	-0.00020	6.41045	0.774464	144.276
7 ²	Whitcomb	2595-6	4.15431	5.36422	-0.00030	5.36392	0.774492	144.285
8	Stewart	2595-6	5.53210	7.14341	-0.00003	7.14338	0.774437	144.268
Average,							0.774464	144.276
9 ²	Whitcomb	2597-8	4.73995	6.12054	0.00000	6.12054	0.774433	144.267
10	Whitcomb	2597-8	4.22430	5.45464	-0.00020	5.45444	0.774470	144.278
11	Stewart	2597-8	5.93271	7.66037	+0.00051	7.66088	0.774416	144.261
Average,							0.774440	144.269
12	Whitcomb	2599-2600	5.60324	7.23524	0.00000	7.23524	0.774439	144.268
13	Stewart	2599-2600	7.22817	9.33324	+0.00035	9.33359	0.774426	144.264
Average,							0.774433	144.266
14	Whitcomb	2601-2	5.16230	6.66582	+0.00020	6.66603	0.774419	144.262
15	Stewart	2601-2	4.50348	5.81508	+0.00050	5.81558	0.774382	144.250
Average,							0.774401	144.256
16	Whitcomb	2603-4	6.42333	8.29438	0.00000	8.29438	0.774419	144.262
17	Stewart	2603-4	7.59534	9.80745	+0.00077	9.80822	0.774385	144.251
Average,							0.774402	144.256

¹ Calculated from the solubility product of silver chloride at 0° as found by Kohlrausch, 9×10^{-12} . *Z. physik. Chem.*, 64, 167 (1908).

² The neodymium chloride used in this experiment was heated almost but not quite to the fusing point.

TABLE II.
The Atomic Weight of Neodymium.
 $\text{NdCl}_3 : 3\text{AgCl}$.
 $\text{Ag} = 107.880$.

No. of anal- yses.	Analyst.	Fraction.	Weight of NdCl_3 in vacuum. Grams.	Weight of AgCl in vacuum. Grams.	Loss on fusion. Gram.	Total dissolved AgCl . Gram.	Corrected weight of AgCl in vacuum. Grams.	Ratio $\text{NdCl}_3 : 3\text{AgCl}$.	Atomic weight of Nd.
18	Stewart	2590-1-2	4.03869	6.92658	0.00048	0.00176	6.92786	0.582963	144.310
19	Whitcomb	2593-4	4.48251	7.68865	0.00016	0.00156	7.69005	0.582897	144.281
20 ¹	Whitcomb	2593-4	3.75204	6.43617	0.00041	0.00162	6.43738	0.582852	144.262
21	Stewart	2593-4	6.00909	10.30826	0.00056	0.00106	10.30876	0.582911	144.287
Average,								0.582887	144.277
22	Whitcomb	2595-6	4.96466	8.51602	0.00033	0.00065	8.51634	0.582957	144.307
23 ¹	Whitcomb	2595-6	4.15431	7.12648	0.00056	0.00151	7.12743	0.582862	144.266
24	Stewart	2595-6	5.53210	9.49047	0.00031	0.00118	9.49134	0.582858	144.264
Average,								0.582892	144.279
25 ¹	Whitcomb	2597-8	4.73995	8.13139	0.00014	0.00107	8.13232	0.582853	144.262
26	Whitcomb	2597-8	4.22430	7.24613	0.00018	0.00119	7.24714	0.582892	144.279
27	Stewart	2597-8	5.93271	10.17821	0.00025	0.00095	10.17891	0.582844	144.258
Average,								0.582863	144.266
28	Whitcomb	2599-2600	5.60325	9.61209	0.00019	0.00109	9.61299	0.582883	144.275
29	Stewart	2599-2600	7.22817	12.40020	0.00024	0.00102	12.40098	0.582871	144.270
Average,								0.582877	144.273
30	Whitcomb	2601-2	5.16230	8.86100	0.00090	0.00137	8.86147	0.582556	(144.134) ²
31	Stewart	2601-2	4.50348	7.72660	0.00025	0.00083	7.72718	0.582810	144.244
32	Whitcomb	2603-4	6.42333	11.02125	0.00078	0.00237	11.02284	0.582729	(144.209) ²

In the analyses by Mr. Stewart, after a similar excess of silver nitrate had been added, the system was allowed to stand at room temperature for several days before filtration. In computing the correction for silver chloride dissolved in the filtrate and silver nitrate washings, which were not chilled, the assumption is made that the solutions were saturated at 25°, since the experiments were carried out during the summer months. Using Kohlrausch's determination of the solubility product of silver chloride at 25°, 1.7×10^{-10} , the solubility in 0.0003 normal silver nitrate is 0.00008 g. The aqueous washings were chilled to diminish the solubility of the precipitate and were analyzed nephelometrically.

The main mass of silver chloride was dried at 150° and the moisture retained was found from the loss on fusion.

¹ The neodymium chloride used in these experiments was heated almost but not quite to the fusing point.

² The results of Analyses 30 and 32 are inexplicably low. As they were the first two experiments carried out by Mr. Whitcomb, we feel that it is justifiable to omit them in the final treatment of the results.

In Mr. Whitcomb's experiments the portions of the original solution removed for nephelometric comparisons were returned and a correction applied for the silver chloride thus introduced. In Mr. Stewart's experiments the test portions were rejected and a correction of 0.00005 g. was added for each 100 cc. of solution removed.

All objects were weighed by substitution for similar counterpoises, a No. 10 Troemner balance being used for the purpose. Weights were standardized to hundredths of a milligram by the Richards' substitution method. The following vacuum corrections were applied:

	Specific gravity.	Vacuum correction per g.
Weights.....	8.3	
NdCl ₃	4.134	+0.000145
AgCl.....	5.56	+0.000071
Ag.....	10.49	-0.000031

TABLE III.

Fraction.	NdCl ₃ :3Ag.	NdCl ₃ :3AgCl.	Average of all analyses.	Corrected average of all analyses.
2590-1-2	144.294	144.310	144.299	144.263
2593-4	144.284	144.277	144.280	144.256
2595-6	144.276	144.279	144.278	144.266
2597-8	144.269	144.266	144.268	144.262
2599-2600	144.266	144.273	144.269	144.269
2601-2	144.256	144.244	144.252	144.254
2603-4	144.256	...	144.256	144.259

Av., 144.261

The results with the different fractions are summarized in Table III, in the last column of which corrections also are made for praseodymium and samarium impurity, on the basis of the atomic weights 140.9 and 150.4, respectively.

Analyses.	Ag:AgCl
2 and 18	0.752678
3 and 19	0.752609
4 and 20	0.752570
5 and 21	0.752653
5 and 22	0.752723
7 and 23	0.752574
8 and 24	0.752621
9 and 25	0.752619
10 and 26	0.752633
11 and 27	0.752623
12 and 28	0.752652
13 and 29	0.752649
14 and 30	(0.752249) ¹
15 and 31	0.752613
16 and 32	(0.752472) ²

Av., 0.752632

¹ THIS JOURNAL, 22, 144 (1900).² See note on page 308.

The concordance of the results with each fraction is satisfactory. It is interesting to note that with the uncorrected results a perceptible difference exists between the head and tail of the series and that this difference largely disappears when corrections are applied for rare earth impurity. The uncorrected results with the purest fractions and the corrected result with all the fractions differ very little from Baxter and Chapin's earlier result, 144.275 ($\text{Ag} = 107.880$).

In the preceding table the ratio of silver used to silver chloride obtained in the same experiment is given for all complete pairs of analyses. Since the average ratio is essentially identical with that found by Richards and Wells,¹ 0.752634, it can reasonably be concluded that errors from occlusion by the silver chloride, or from loss of silver chloride, are absent. This is in accord with earlier experience of the same kind.

Summary.

Neodymium nitrate was purified by fractional crystallization of the nitrate from concentrated nitric acid. Chloride, prepared from the final fractions of nitrate, was analyzed by comparison with silver. The atomic weight of neodymium was thus found to be 144.261. The average of this result and that found earlier by Baxter and Chapin, 144.275, is 144.268. The rounded-off figure 144.27 ($\text{Ag} = 107.88$) seems to represent fairly the final outcome of both researches.

We are very greatly indebted to the Carnegie Institution of Washington for generous pecuniary assistance, as well as to Dr. H. S. Miner, of the Welsbach Light Company, for the neodymium material.

CAMBRIDGE, MASS.

THE SOLUBILITIES OF THE SULFATES OF BARIUM, STRONTIUM, CALCIUM AND LEAD IN AMMONIUM ACETATE SOLUTIONS AT 25° AND A CRITICISM OF THE PRESENT METHODS FOR THE SEPARATION OF THESE SUBSTANCES BY MEANS OF AMMONIUM ACETATE SOLUTIONS.

By J. W. MARDEN.

Received November 18, 1915.

In the last few years several attempts have been made to separate lead sulfate from the other sulfates which are relatively insoluble in water by the use of ammonium acetate solution. Such a method, where lead sulfate could be completely separated from the sulfates of barium, strontium and calcium, would be of value both in qualitative and quantitative analysis.

Qualitative statements of the solubilities of the four sulfates occur frequently in chemical literature. In the case of lead sulfate it is the general

¹ *Publ. Carnegie Inst.*, No. 28, 1905; *THIS JOURNAL*, 28, 456 (1908).

consensus of opinion that it dissolves to a considerable extent in ammonium acetate solutions. Bolley¹ gives the solubility at 12.5° as 1 part in 47 parts of ammonium acetate of specific gravity 1.036 (about 16% solution). Noyes and Whitcomb² have given the solubilities of lead sulfate in dilute solutions of ammonium acetate at 25° and Dunnington and Long³ have published the solubilities of lead sulfate in fairly concentrated solutions at 100°.

According to Storer, calcium sulfate is soluble to a very considerable extent in an aqueous solution of acetate of ammonium at 18–25° and is quite soluble in solutions of other ammonium salts. Cameron and Brown⁴ have found that the solubility of calcium sulfate is greater in ammonium nitrate and ammonium chloride solutions than in pure water. As far back as 1823⁵ at least, the solubility of strontium sulfate was in dispute. A method for the separation of the sulfate of strontium from that of barium was based upon the solubilities of the sulfates in water. Smithson found, however, that he could get no precipitate with sodium carbonate in the filtrate from a water solution of sodium sulfate in which the sulfate of strontium had lain long. Most of the early authors considered strontium sulfate completely insoluble in solutions of ammonium salts, but at the same time admitted that the ammonium salts of the organic acids interfere with its precipitation. According to Storer, also, the sulfate of barium is soluble to a considerable extent in aqueous solutions of certain ammonium salts. He also states that the precipitation of barium sulfate is prevented by the presence of ammonium citrate, etc.

Curtman and Frankel⁶ suggest a qualitative method where they "have devised a scheme of analysis, by which small amounts of alkaline earth metals may be detected. The method consists in the precipitation of the alkaline earth metals together with a part of the lead as sulfates, with dilute sulfuric acid and alcohol from a solution of definite acidity. After extracting the lead sulfate with ammonium acetate, the alkaline earth sulfates are converted to carbonates by boiling with sodium carbonate solution. The carbonates are then dissolved in acetic acid and the resulting solutions analyzed in the usual manner."

In the face of such conflicting statements, on the one hand by Curtman and Frankel that good results are obtained by their method, and on the other hand the statements indicating that calcium and barium sulfates are somewhat soluble in ammonium salts, it was thought that it would be

¹ Storer, "Dictionary of Solubilities of Chem. Substances," Cambridge, 1864.

² THIS JOURNAL, 27, 756 (1905).

³ *Am. Chem. J.*, 22, 217 (1899).

⁴ *J. Phys. Chem.*, 9, 210 (1905).

⁵ Smithsonian Collection, *Misc.*, 21, 81 (1879).

⁶ THIS JOURNAL, 34, 1493 (1912).

profitable to determine the solubilities of these substances in ammonium acetate solutions.

The ammonium acetate solutions for this work were prepared much as Noyes and Whitcomb have suggested. A standard HCl solution was made by precipitating and weighing silver chloride in the usual manner and a sodium hydroxide solution was standardized by titration with this acid. The ammonium hydroxide was standardized against the HCl with methyl orange as the indicator and the acetic acid (prepared by diluting the glacial acid) was standardized against the sodium hydroxide with phenolphthalein as the indicator. The titrations were all made by weight. The exact weights of ammonium hydroxide and acetic acid solutions were calculated and mixed carefully so as to get a "neutral" solution. A solution was prepared in this way which contained 21.37 g. of ammonium acetate per 100 g. of solution. The more dilute solutions were made by adding weighed portions of water.

The sulfates were purified material. In each case they were treated with water, filtered and washed repeatedly on a Büchner funnel to remove any soluble impurities. These operations were repeated twice. In the case of calcium sulfate a trace of carbonate was found which was destroyed with a little sulfuric acid in the first wash water.

In determining the solubilities, the solutions were saturated by shaking in a thermostat with a large excess of the solid sulfate for twelve to sixteen hours. In some cases the value was obtained by starting with either super-saturated or undersaturated solutions, while in other cases, when it had been proved that twelve hours was sufficient time for saturation, duplicate determinations were taken, one after twelve hours' shaking and the other after sixteen hours' shaking in the thermostat, starting with unsaturated solutions.

The sulfates in the saturated ammonium acetate solutions were determined directly by placing weighed portions of the solution in platinum dishes, evaporating to a few cc. on the water bath, adding a few drops of concentrated sulfuric acid and heating very cautiously until the ammonium sulfate thus formed and the excess of acid were removed, leaving the sulfate of the metal under test. Blanks were run on the method of determination and it was found that any one of the sulfates could be put through this process without any appreciable loss. The nonvolatile residue due to the solubilities of the glass of the bottles and the residue of the ammonium acetate was very little, less than 0.0005 g. in each case tried.

The specific gravities of the ammonium acetate solutions were determined at 25°, so that the solubility results given below can be calculated either by weight or by volume. The concentrations of the ammonium acetate in Table I and in the following tables are in terms of grams per 100 g. of ammonium acetate solution.

TABLE I.

Conc. of ammonium acetate.....	2.13	5.34	10.68	16.02	21.37
Sp. gr.....	1.005	1.012	1.024	1.036	1.045

These values are very nearly the same as those obtained by Hager¹ at 16°.

Table II gives the grams of lead sulfate soluble in 100 grams of ammonium acetate solutions at 25°. The first four values have been calculated from the data of Noyes and Whitcomb.²

TABLE II.

Conc. of ammonium acetate.....	0.000	0.796	1.591	3.170	5.34	10.68	21.37
Grams of lead sulfate.....	0.0041	0.0636	0.137	0.304	0.56	1.68	3.89

The solubilities of calcium sulfate in ammonium acetate solutions at 25° are given in Table III.

TABLE III.

Conc. of ammonium acetate.....	0.00	2.13	5.34	10.68	21.37
Grams of calcium sulfate.....	0.2085 ³	0.454	0.752	1.146	1.755

Table IV shows the solubilities of strontium sulfate in ammonium acetate solution of various strengths at 25°.

TABLE IV.

Conc. of ammonium acetate.....	0.00	2.13	5.34	10.68	21.37
Grams of strontium sulfate.....	0.0151 ⁴	0.0451	0.0732	0.0942	0.115

The solubilities of barium sulfate at 25° in water and in one concentration of ammonium acetate are given in Table V.

TABLE V.

Conc. of ammonium acetate.....	0.00	21.37
Grams of barium sulfate.....	0.00023 ⁵	0.016

When these values are plotted together on the same diagram, the curves indicate that at 25° the more concentrated the ammonium acetate solution the better will be the separation of the lead sulfate from the others. It is to be noted, however, that the solubilities, even of the barium and strontium sulfates, are considerable in ammonium acetate solution as compared to their solubilities in water. Also, it might be pointed out that no definite separation for the calcium sulfate could be made with ammonium acetate solution at ordinary temperatures.

In the qualitative method of separation of the sulfate suggested by Curtman and Frankel, "the precipitate of washed sulfates is (then) treated with a hot solution of ammonium acetate, until the extract no longer gives a test for lead with sulfuric acid." To get an idea of the solubilities of the sulfates in hot ammonium acetate solutions, each of the sulfates was di-

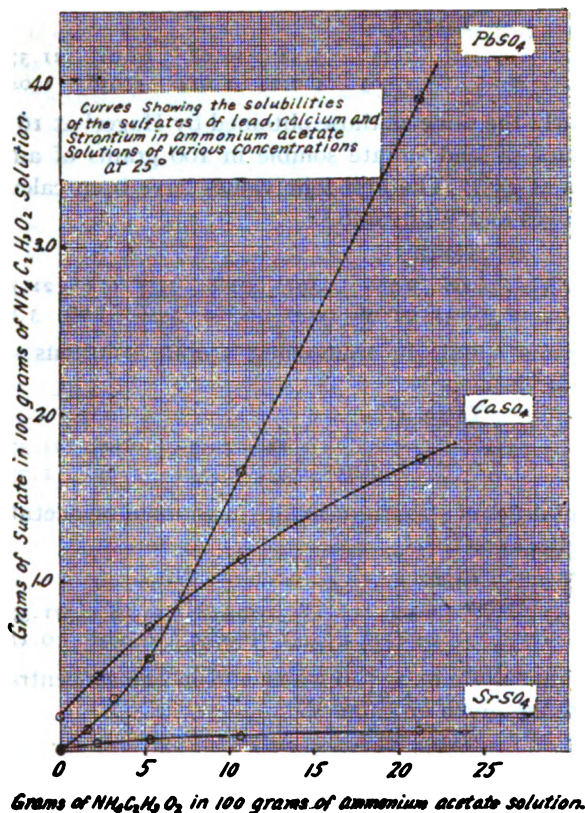
¹ "Manule Pharmaceuticum adjumenta varia," Leipsig, 1876.

² THIS JOURNAL, 24, 667 (1902).

³ Hulett and Allen, THIS JOURNAL, 24, 667 (1902).

⁴ Wolfman, *Osterr.-ung. Z. Zuckerind.*, 25, 988 (1896).

⁵ Hulett, *Z. physik. Chem.*, 37, 398 (1901).



gested very gently at 100° in a 3 N solution of ammonium acetate for just ten minutes, a portion of the clear filtrate weighed out in a platinum dish evaporated nearly to dryness, cooled and the residue treated with a little sulfuric acid, ignited and weighed. Table VI shows the weights of the sulfates dissolved in this way in 100 grams of 3 N ammonium acetate solution. These tests are, to be sure, rough, but they will partially duplicate the conditions described above and will give an idea of the amounts which dissolve under these conditions.

TABLE VI.

Substance.	Weight of sulfate.
Barium sulfate.....	0.025
Strontium sulfate.....	0.142
Calcium sulfate.....	2.60
Lead sulfate.....	6.15

At first sight it would seem impossible to get very delicate results in testing for strontium if much ammonium acetate solution is used in washing the sulfates. A little experience indicated, however, that if the ammonium acetate solution contained a small amount of some soluble sulfate the solubilities of the barium and strontium sulfates were reduced. In 100 g. of 3 N ammonium acetate solution to which 1% of ammonium sulfate had been added the following amounts of sulfates were dissolved when treated in the same way as above at 100°.

TABLE VII.

Substance.	Weight of sulfate.
Barium sulfate.....	0.004
Strontium sulfate.....	0.010
Calcium sulfate.....	2.31
Lead sulfate.....	5.75

The addition of 1% of ammonium sulfate to the ammonium acetate solution diminishes the solubilities of barium and strontium sulfates enough for a qualitative separation, while larger amounts of calcium and lead sulfates are still soluble. We can, knowing this, explain why Curtman and Frankel obtained such good results in testing their method of analysis. They obtained conclusive tests for as little as 1 to 2 mg. of barium and strontium but admitted that in one or two cases where only 1 mg. of strontium was present the tests were faint. Curtman and Frankel made very few tests on small amounts of barium and strontium in absence of other sulfates the presence of which would lessen the solubility of the former. When several trials were made by their method, digesting the sulfates for ten minutes in 20 cc. of 3 *N* solution of ammonium acetate at 100° and washing the residue on the filter paper with a few cc. of the same hot solution, it took nearly 20 mg. of strontium to give a good test, if the other sulfates were not present. If a fairly large amount of the other sulfates like those of lead and calcium were present accurate results, such as the Curtman and Frankel table shows, could be obtained. The solubilities of the sulfates, when only washed on a filter paper with boiling hot ammonium acetate solution, were found to be smaller than when they were digested in the solution at 100° for ten minutes, but the values of the solubilities of the calcium and lead bore the same ratio to those of barium and strontium as before.

If a 3 *N* ammonium acetate solution containing 1% of ammonium sulfate was used for the solvent instead of ammonium acetate alone, conclusive tests were obtained for as little as 3-5 mg. of strontium, calcium or lead and 1 to 2 mg. of barium, regardless of whether the other sulfates were present or not.

A modification of Curtman and Frankel's method is being used by Prof. J. A. Gibson¹ of this laboratory in his course in qualitative analysis. He uses the method immediately following the precipitation of the HCl group. He found, when alcohol was used to aid the precipitation of the sulfates, that occasionally a yellow precipitate appeared. This, according to Treadwell,² is a basic mercuric sulfate which is easily dissolved upon the addition of a small amount of dilute HCl.

A modification of Gibson's method is given below by the use of which a student should be able to identify with certainty a few milligrams of barium, strontium, lead and calcium. The calcium, if there is only a small amount present in the original solution, will be detected by ammonium oxalate either after removing the lead from the material soluble in ammonium acetate or after the ammonium sulfide separation.

¹ "A System of Qualitative Analysis," Univ. of Mo., 1914.

² Treadwell and Hall, "Analytical Chemistry," Vol. 1, 148 (1911), John Wiley and Sons, New York.

Procedure.

If the volume of the solution is large, boil down to about 20 cc., add 3 cc. of 2 *N* sulfuric acid and an equal volume of ethyl alcohol. Let stand five minutes and filter. Wash twice with (1-1) alcohol-water mixture.

Wash the precipitated sulfates five times with a boiling 3 *N* ammonium acetate solution containing 1% of ammonium sulfate, using a wash bottle and allowing 5 cc. of ammonium acetate solution for each washing. Catch the filtrate in a porcelain dish.

Evaporate the ammonium acetate filtrate over a water bath to a sirupy consistency, cool, add concentrated sulfuric acid drop by drop (about 1 cc.) and dry the residue on the water bath. Heat the dish gently at first and then to a dull red later over the free flame to remove the ammonium sulfate and the sulfuric acid. Cool, put 5 to 10 cc. of normal sodium hydroxide solution in the dish and rub the residue with a stirring rod to loosen it. Filter the sodium hydroxide solution and make the filtrate acid with acetic acid. Add a few drops of potassium chromate solution; a yellow precipitate indicates the presence of lead.

The barium and strontium sulfates are converted to the carbonates by boiling in 4 *N* sodium carbonate solution and tested in the usual manner.

If a yellow precipitate comes down when the sulfuric acid and alcohol are added, add dilute HCl drop by drop with shaking till the yellow precipitate disappears. Accuracy cannot be attained if too much HCl is used in precipitation of the silver group.

In testing this method very good results were obtained, either when the sulfates were alone in the solution or when other groups were present.

A number of quantitative methods have been suggested for the separation of lead sulfate from the other sulfates by dissolving it in ammonium acetate solution. Leach,¹ for example, has suggested the determination of small amounts of lead in soft drinks by sulfating the ash and dissolving out the lead sulfate with ammonium acetate solution. The lead is subsequently determined colorimetrically with hydrogen sulfide. With this method probably there would be difficulty if copper or tin sulfates were in the sulfated ash, for these substances would go with the lead into the ammonium acetate solution.

No matter which method is used, if lead is to be determined by separating the sulfate from other substances by means of ammonium acetate solution, the ammonium acetate must first be removed before the lead thus obtained can be precipitated with accuracy.

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¹ "Food Inspection and Analysis," 1906, p. 704, John Wiley and Sons, New York.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN.]

THE EFFECT OF DISSOLVED SUBSTANCES ON THE VELOCITY OF CRYSTALLIZATION OF WATER.

By JAMES H. WALTON AND ALBERT BRAUN.

Received December 8, 1915.

The measurement of the speed of crystallization of undercooled water has been described in a previous communication.¹ The linear velocity of crystallization (hereafter designated as V. C.) was measured to -9° . It was shown that the internal diameter of the tube and the thickness of its walls are important factors in the rate of growth of the crystals.

Inasmuch as no investigation has been made on the influence of foreign substances on the V. C. of water, it was considered of interest and importance to determine the effect of various types of dissolved substances on the rate with which ice crystals are formed.

Historical.

The general subject of the effect of foreign substances on the V. C. of undercooled liquids has already been the field of numerous investigations. One of the best known researches on this subject was carried out by von Pickardt,² who dissolved various organic compounds in fused benzophenone and determined their influence on the V. C. of this substance. He came to the following conclusions:

1. That all dissolved substances lower the V. C.
2. The decrease in the V. C. is proportional to the square root of the concentration of the dissolved substance.
3. In equimolecular concentrations of different substances the lowering of the V. C. is the same.

The conclusions of this investigation are questioned by Padoa and Galeati,³ and also by Dreyer.⁴ The former increased the number of dissolved substances used and found that out of thirty-two cases investigated, three agreed with von Pickardt's rule, twelve were in fairly good agreement, seven approximated it, and ten showed no relation whatever. The investigations of Dreyer with undercooled formanilide showed similar disagreements between the V. C., and the molecular weight of the solutes used. Dreyer found that when ethyl or methyl alcohol was used each actually *increased* the V. C. of the formanilide. The influence of the solute upon the V. C. of undercooled liquids, therefore, is specific.

Tammann⁵ has carried out experiments showing the relation between the temperature and the V. C. of various undercooled liquids. The

¹ *J. Phys. Chem.*, 18, 722 (1914).

² *Z. physik. Chem.*, 42, 17 (1902).

³ *Gazz. chim. ital.*, 35, I, 181 (1904).

⁴ *Z. physik. Chem.*, 48, 467 (1904).

⁵ "Kristallisieren und Schmelzen," 1907, p. 131.

speed of crystallization at first increases with increased undercooling (Zone A); it then generally remains constant for several degrees (Zone B) and finally decreases (Zone C). For benzophenone Zone A extends from 48° , the melting point of this substance, to 25° . The maximum V. C., Zone B, takes place from 25° to about -20° . It is obvious that in this region the V. C. is independent of the temperature. Below -20° the V. C. decreases with the fall in temperature. The experiments of von Pickardt and of Padoa and Galeati were carried out in the zone of the maximum V. C.

The V. C. from supersaturated solutions has been the subject of exhaustive investigations by Marc,¹ who completely eliminated the velocity of diffusion in his experiments, and measured the true speed of crystallization from aqueous solutions. The V. C. was decreased by the presence of many dissolved substances, dyes, for examples, being particularly operative in this respect. Marc came to the conclusion that the inhibition of the crystallization is an adsorption effect, being due in this particular case to adsorption of the dye on the surface of the crystal. The adsorption is supposed to affect the V. C. as follows: The substance that is being separated from the supersaturated solution is adsorbed at the surface of the crystal, consequently at that point there is a greater supersaturation than in the other parts of the solution. The concentration of this adsorbed layer determines the V. C. If other substances capable of being adsorbed are present in the solution, the concentration of the crystallizing substance in the surface layer is thereby decreased, and consequently the V. C. is retarded.

Freundlich² believes that the V. C. of undercooled liquids can also be explained by adsorption phenomena. A study of the experiments of von Pickardt and Padoa and Galeati led him to the following conclusions:

1. The decrease of the maximum V. C. of undercooled liquids by foreign substances, present in not too great concentration, may be expressed by the equation

$$G_0 - G = kc^{1/n}.$$

In this equation G_0 = V. C. of pure fusion; G = V. C. of impure fusion; c = concentration of the dissolved substance; k and $1/n$ are constants, the value of $1/n$ lying between 0.2 and 0.7.

2. The equation may be explained by the assumption that the dissolved substance is adsorbed on the surface of the crystal and this results in decreasing the V. C. in proportion to the amount adsorbed.

The formula used by Freundlich is the well-known adsorption formula, and is the same as that used by von Pickardt. The latter assumed the

¹ *Z. physik. Chem.*, 61, 385 (1908); 67, 470 (1909); 68, 104 (1909); 73, 685 (1910); 75, 710 (1910).

² *Ibid.*, 75, 245 (1910).

value of $1/n$ to be 0.5, but this assumption is not borne out by experiment. Its value is variable, depending on the specific nature of the substance in the fusion. Freundlich states that, while the V. C. depends upon adsorption of the dissolved impurity, there are doubtless other factors that influence it in a large degree.

Experimental.

Method.—The method used in these experiments was to introduce into a constant low temperature bath,¹ an L-shaped tube that contained the solution to be undercooled. The dimensions of the tubes were practically the same as those used in the determination of the V. C. of undercooled water, the outside diameter being about 12 mm., and the bore about 7 mm. After the tube had arrived at the temperature of its surroundings, which took 3–4 minutes, it was inoculated, and the time necessary for the crystal growth to progress a distance of one meter in the tube was measured by a stop watch.

In preparing the solutions the purest chemicals obtainable were employed. In several cases these were recrystallized, but this was found to be unnecessary, as the error caused by any trace of impurity in these substances was found to be well within the error of the experiments. In the preparation of the solutions, conductivity water was used. Whenever possible, the solutions were boiled to remove any dissolved gases. The surface of the liquid was then covered with a half-inch layer of paraffin oil, and the tube kept in ice water until ready to be placed in the low temperature bath.

TABLE I.

Showing the agreement of duplicate measurements of the velocity of crystallization of typical undercooled aqueous solutions. Temperature -9.1° .

Solution.	Tube.	Time in seconds per meter.		
Cane sugar.....	10	69.9	69.9	71
Cane sugar.....	12	71	68.0	70
Cane sugar.....	6	75.4	75.1	75.2
Urea.....	10	20.0	20.5	20.3
Urea.....	12	18.4	19.1	18.3
Succinic acid.....	10	31.4	33.5	..
Succinic acid.....	1	36.8	37.0	35.4
Cupric chloride.....	10	40	40.0	..
Cupric chloride.....	14	..	39.5	..
Dextrose.....	14	87.8	86.4	..
Dextrose.....	1	78.4	77.0	..
Mannose.....	14	85	83.4	..
Mannose.....	4	86.5	85.2	..
Sodium sulfate.....	14	29.6	29.3	29.0
Sodium hydroxide.....	14	22.6	21.8	..
Sodium hydroxide.....	12	..	22.4	..

¹ *J. Phys. Chem.*, 18, 717 (1914).

The velocity of crystallization was determined several times with the same tubes. After one determination had been made the ice was melted by placing the tube in a bath heated to about 60° and allowing it to remain there for ten or fifteen minutes. By heating the tube to this temperature there seems to be less of a tendency for the solution to crystallize spontaneously. As will be shown later, however, the occurrence of spontaneous crystallization seems to depend largely on the nature of the substance in solution.

TABLE II.

The linear velocity of crystallization of 0.1 *M* undercooled aqueous solutions.
Temperature -9.1° .

Compound.	Formula.	Mol. wt. of anhydrous substance.	No. atoms in mol. of substance.	Time per meter. Seconds.	Velocity cm. per min.
Pure water.....	H ₂ O	18.0	..	16.3	368
Lithium chloride ¹	LiCl	42.5	2	35.3	170
Potassium iodide.....	KI	166.0	2	26.1	230
Sodium chloride.....	NaCl	58.5	2	24.3	247
Hydrochloric acid ²	HCl	36.5	2	24.0	250
Cupric chloride.....	CuCl ₂	134.6	3	40.0	150
Mercuric chloride.....	HgCl ₂	271.6	3	27.7	217
Calcium chloride.....	CaCl ₂	111.7	3	38.6	155
Sodium hydroxide.....	NaOH	40.0	3	21.9	274
Ferric chloride.....	FeCl ₃	162.5	4	84.8	70.8
Hydrogen peroxide.....	H ₂ O ₂	34.0	4	24.1	248
Potassium chlorate.....	KClO ₃	122.6	5	26.2	229
Mercuric cyanide.....	Hg(CN) ₂	252.0	5	23.4	256
Silver nitrate.....	AgNO ₃	169.8	5	22.5	267
Sodium carbonate.....	Na ₂ CO ₃	106.0	6	33.3	180
Sulfuric acid ¹	H ₂ SO ₄	98.0	7	28.7	209
Potassium sulfate.....	K ₂ SO ₄	174.0	7	23.4	256
Sodium sulfate.....	Na ₂ SO ₄	142.0	7	29.2	205
Urea.....	CO(NH ₂) ₂	60.0	8	19.1	314
Ethyl alcohol.....	C ₂ H ₅ OH	46.0	9	34.0	177
Potassium dichromate.....	K ₂ Cr ₂ O ₇	294.2	11	31.1	194
Succinic acid ²	C ₄ H ₄ O ₄	118.0	14	35.3	170
Glycerol ¹	C ₃ H ₈ O ₃	92.0	14	33.6	176
Tartaric acid.....	C ₄ H ₄ O ₆	150.0	16	43.4	138
Mannose ³	C ₆ H ₁₂ O ₆	180.0	24	83.6	71.8
Dextrose ³	C ₆ H ₁₂ O ₆	180.0	24	82.3	72.9
Fructose.....	C ₆ H ₁₂ O ₆	180.0	24	86.5	78.4
Antipyrine.....	C ₁₁ H ₁₂ N ₂ O	188.0	26	53.7	112
Cane sugar ¹	C ₁₂ H ₂₂ O ₁₁	342.0	45	152.0	39.5
Lactose ²	C ₁₂ H ₂₂ O ₁₁	342.0	45	178.8	33.6
Raffinose.....	C ₁₈ H ₃₂ O ₁₆	344.0	56	215.5	27.8

¹ Shows great tendency to crystallize spontaneously.

² Little tendency to crystallize spontaneously.

³ Appearance of crystals different from those separating from undercooled water.

The Velocity of Crystallization of 0.1 *M* and 0.02 *M* Solutions.—In the first series of experiments 0.1 *M* solutions of typical salts, alkalies, acids, and a number of organic compounds were used. The substances used and the results obtained are given in Table II. A number of other compounds were used, among which were copper nitrate, magnesium sulfate, castile soap, gelatin, gum arabic, and egg albumin, but no results were obtained because the solutions always crystallized spontaneously. The results contained in Table II are the average of three or more determinations.

Table I gives results obtained from repeated measurements with solutions using the same tube. The agreement of different tubes containing the same solution is also given.

Because of spontaneous crystallization many of the results in Table II were obtained only after repeated trials. Cane sugar shows this tendency to a marked degree. Hydrochloric acid solutions on the other hand proved to be very stable and were kept at -9° , in one case, for half an hour. With a few exceptions the appearance of the crystals formed was the same with the solution as with pure water.

A series of experiments was carried out in which the substances used have a very high molecular weight. Inasmuch as many of the compounds are not sufficiently soluble to permit the preparation of 0.1 *M* solutions, the concentration used was 0.02 *M*. The results of these experiments are incorporated in Table III.

TABLE III.

The linear velocity of crystallization of 0.02 *M* undercooled aqueous solutions.
Temperature -9.1° .

Compound.	Formula.	Mol. wt. of anhyd. subs.	No. atoms in mol. of anhyd. subs.	Time per meter in seconds.	Velocity.
Hydrochloric acid.....	HCl	36.5	2	15.8	380
Succinic acid.....	$C_4H_6O_4$	118.0	14	19.7	305
Tannic acid.....	$C_{14}H_{10}O_8$	322.0	33	18.3	327
Cocaine hydrochloride...	$C_{17}H_{21}NO_4 \cdot HCl$	339.5	45	28.0	214
Lactose.....	$C_{12}H_{22}O_{11}$	342.0	45	26.3	228
Quinine hydrochloride...	$C_{20}H_{24}N_2O_8 \cdot 2HCl$	397.0	52	31.5	190
Quinine bisulfate.....	$(C_{20}H_{24}N_2O_8) \cdot H_2SO_4$	422.0	55	33.5	180
Raffinose.....	$C_{18}H_{34}O_{16}$	344.0	56	29.0	207
Brucine sulfate.....	$(C_{23}H_{28}N_4O_8) \cdot H_2SO_4$	886.0	115	53.0	118

The experiments of von Pickardt, Dreyer and Freundlich, to which reference has been made, were carried out in the zone of maximum V. C. This could not be done in the experiments described in this paper, for spontaneous crystallization made it impossible to determine the rate of crystallization in Zone B, which should be about twenty degrees below the freezing point. The lowest temperature obtainable was about 9° below the melting point of ice. Measurements carried out in this

zone cannot, therefore, be considered as the true velocity of crystallization. They are of value, however, in showing the relative effects of equimolecular solutions of different types of compounds. Since the V. C. in the temperature zone in which these measurements were made increases with the degree of undercooling, the lowering of the freezing point by the addition of the solute would have an appreciable influence upon the retardation of the V. C. For it is plain that a 0.1 *M* solution at -9° is not undercooled as much as the pure solvent at this temperature, a normal solution of hydrochloric acid, for example, would be undercooled but 5° .¹ This would result in a great difference in the V. C. of the acid and pure water. To eliminate the effects of different amounts of undercooling equimolecular solutions were used in these experiments. A 0.1 *M* solution of a strongly dissociated substance, such as hydrochloric acid, however, has a lower freezing point than a 0.1 *M* solution of a nondissociated substance like cane sugar. At -9° these two solutions are not equally undercooled. An examination of Fig. 1, and Table VI, which give the

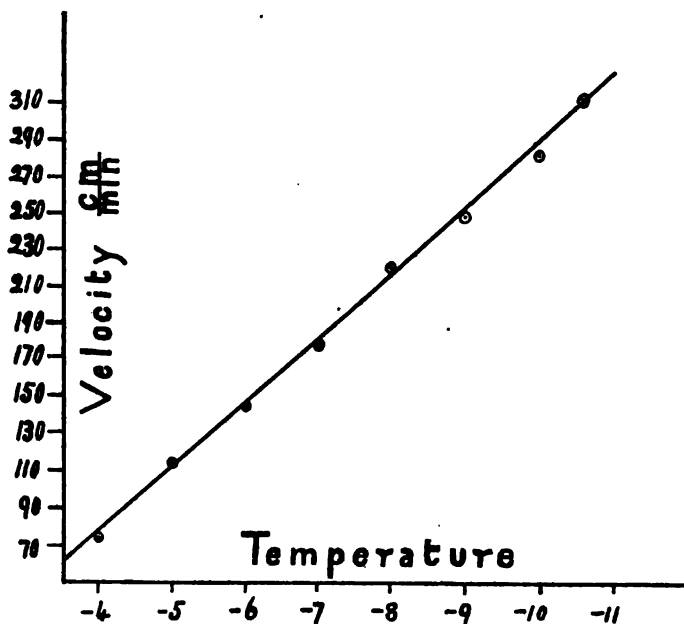


Fig. 1.

changes in velocity in 0.1 *M* solutions of hydrochloric acid for changes of temperature, shows that at -9° the velocity of crystallization is 246, while at -10° it is about 280 cm. per minute. The error caused by this difference in the amount of undercooling would, therefore, be negligible.

¹ Richards and Jackson, *Z. physik. Chem.*, 56, 362 (1906).

Discussion of Results.—The results obtained with 0.1 *M* solutions as given in Table II show that there is no relation between the molecular weight of a compound and its retardation of the V. C. of the water. Mercuric chloride with a molecular weight of 271.6 has about the same retarding effect as sulfuric acid (mol. wt. 98). Ferric chloride and potassium iodide have approximately the same molecular weights, yet the velocity of crystallization with the former is 70.7; with the iodide it is 230 cm. per minute. A similar difference is seen in the case of potassium sulfate and glucose. The most striking relation, however, is that which exists between the number of atoms in the compound and the velocity of crystallization of the solution. The results in Table II are arranged with reference to the increase of numbers of atoms in the molecule. An examination of the compounds with more than eight atoms in the molecule shows that the number of atoms is one of the factors that determines the retarding effect of that compound on the V. C. The relation is only an approximate one, to be sure, but that such a relation does exist is evident in the case of compounds with more than eight atoms to the molecule. In the case of simpler inorganic compounds there are many exceptions. Lithium chloride and ethyl alcohol, for example, have the same V. C., although the former has two atoms, the latter nine. For compounds below ethyl alcohol the increase of the inhibiting effect with the increase in number of atoms in the compound, is fairly regular. The fact that ethyl alcohol was found by Dreyer to accelerate the V. C. of formanilide, while here it retards the formation of crystals, is worthy of note.

The results given in Table III show the effect of 0.02 *M* solutions at -9° . The same relation between the increase in the number of atoms in the molecule and the retarding of the V. C. can also be seen from these experiments.

The explanation of the inhibitive action of these compounds cannot be due primarily to adsorption, as claimed by Freundlich in the retardation of the crystallization of benzophenone by impurities.

Freundlich points out that compounds that have a large number of atoms retard the crystallization of benzophenone to a marked degree. Isobidesyl, $C_{20}H_{22}O_2$, and lepiden, $C_{28}H_{30}O$, showed a very great retarding effect not only with benzophenone but also with diphenylamine and α -naphthylamine. This is considered by Freundlich to be due to the fact that these compounds are very strongly adsorbed. He makes the following statement:

"Allerdings sind die Abweichungen bei der Beeinflussung der Kristallisationsgeschwindigkeit durch gelöste Stoffe schon häufig und gross genug. Es entspricht durchaus dem, was sonst von der Adsorption bekannt ist, dass gerade die hochmolekularen Stoffe, wie Lepiden und Isobidesyl, die Kristallisationsgeschwindigkeit besonders stark herabsetzen, also stark adsorbiert werden."

That the greater adsorption of the high molecular compounds cannot in the present investigation be the explanation of the retarding effect is shown in Table II by the V. C. of the undercooled solutions, containing the sugars. These substances retard the V. C. but they are not greatly adsorbed.

"Die Halogene gehören zu den stark adsorbierbaren, Rohrzucker (und voraussichtlich alle stark hydroxylhaltigen Stoffe) zu den Schwach adsorbierbaren Stoffe."¹

Succinic acid, moreover, has a greater V. C. (170) than tartaric (138.3) which has two hydroxyl groups in the molecule. The alkaloids, however, have a marked retarding effect on the V. C. and they are also known to be strongly adsorbed. They are the only strong retarders that show this relation.

While there is no regularity in the behavior of the compounds with less than eight atoms to the molecule, from the knowledge of adsorption that we possess it is evident that in this case also the phenomenon of adsorption plays a negligible role. Concerning the extent to which certain inorganic salts are adsorbed Freundlich² makes the following statement:

"Nach unveröffentlichten Versuchen von Morawitz, adsorbiert Blutkohle die anorganischen Salze der Alkali und Erdalkalimetalle so wenig, dass es besonderer analytischer Hilfsmittel bedürfen würde um unzweideutig Sinn und Grösse der adsorbierten Menge festzustellen. Dagegen werden die Salze der Schwermetalle (CuSO_4 , AgNO_3 , HgCl_2) ganz merkbar positiv adsorbiert."

When the V. C. of salts of alkalis and alkaline earths are compared with the V. C. of salts of the heavy metals it is seen that adsorption plays an insignificant role.

(1) V. C. of CaCl_2 155; NaCl , 247.

(2) V. C. of CuCl_2 150; HgCl_2 , 218; AgNO_3 , 267.

In the light of the foregoing statement by Freundlich the salts under (2) are adsorbed much more than those under (1) and as a consequence should retard the V. C. much more. A comparison of calcium chloride with the chlorides of copper and mercury, and of sodium chloride with silver nitrate shows that this is not the case.

While the decrease in the velocity of crystallization of water cannot be explained by the assumption that the dissolved substances are adsorbed in different amounts at the crystal surfaces, on the other hand the data which have been obtained in these experiments do not permit any explanation of this phenomenon. The similarity between the velocity of formation of crystals and some of the well-known reactions in chemical kinetics, however, is very suggestive.

O. Lehmann³ has pointed out that an undercooled liquid is by no means a collection of similar molecules, but is composed of different molecular

¹ Freundlich, "Kapillarchemie," 1909, p. 160.

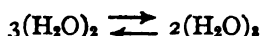
² "Kapillarchemie," 1909, p. 166.

³ "Molekularphysik," 1888, I, p. 683 (Erstarren und Schmelzen).

aggregates in a state of equilibrium. Only one type of these molecular aggregates, M_c , is capable of crystallizing, and this is in equilibrium with the other molecules in the fusion M_f . The state of equilibrium would then be expressed by the equation



That water in the neighborhood of its freezing point consists of such molecular aggregates is a generally accepted fact. Sutherland¹ believes liquid water to be a mixture of dihydrol $(H_2O)_2$, and trihydrol $(H_2O)_3$, the latter compound at 0° being present to the extent of 37.5%. The formation of ice crystals may consequently be considered as an increase in the more complex molecular aggregates and may be represented by an equation similar to the following:



That the presence of foreign substances should influence the rate at which the above change takes place is a reasonable assumption.

Smith² and his co-workers have shown that at the melting point of monoclinic sulfur a similar case of equilibrium exists. The liquid contains two molecular aggregates, S_{16} , (S_8) and the monoclinic sulfur S_8 , (S_8) . The rate at which equilibrium between these two forms is attained is accelerated by certain reagents; by others it is retarded. Ammonia acts as an accelerator, sulfur dioxide as a retarder.

That the effect of the dissolved substances on the speed of the reaction between di- and trihydrol should be specific, is not surprising; it is, in fact, to be expected. Just why all these compounds retard the V. C., instead of accelerating the reaction, is a fact that is difficult to explain. It is of interest in this connection to point out that among the simpler compounds, those that show an unusual retarding effect belong for the greater part to one type, *viz.*, those that either crystallize with water of crystallization or are very deliquescent. There are one or two exceptions to be sure, but lithium chloride, copper chloride, calcium chloride, sodium carbonate and especially ferric chloride show an inhibiting action that is abnormal. The attraction that these substances have for water may have a relation to the unusual retarding effect³ that they have upon the rate at which the molecules undergo rearrangement. The reason why the molecules with a large number of atoms show such an unusual retarding effect is difficult to explain. Certain it is this cannot be due to the fact that they are adsorbed to a greater extent than the simpler compounds.

¹ *Phil. Mag.*, [16] 50, 460 (1900).

² *THIS JOURNAL*, 27, 797 (1905); 29, 499 (1907).

³ An article by Jones and one of his co-workers, published in a recent number of *THIS JOURNAL*, 38, 105 (1916), is of interest in this connection. These investigators showed that "Salts with water of crystallization increase the velocity of the saponifica-

Change of Crystal Habit.—It has long been known that the speed of crystallization is often retarded by substances that change the crystal habit. A possible explanation of the inhibiting effect of various solutes may lie in the fact that these substances change the kind of ice crystals, and consequently the speed at which they are separated from the solution. Mention has already been made of the fact that the crystals liberated from solution of hydrochloric acid and certain of the sugar solutions were different in appearance from the crystals formed with pure water, although with most of the solutions used, the appearance of the crystals was the same as those obtained with water. Hartmann¹ found that four kinds of crystals were separated from undercooled solutions of the following compounds: cane sugar; MnSO_4 ; $\text{HC}_2\text{H}_3\text{O}_2$; NaOH ; $\text{C}_2\text{H}_5(\text{OH})_2$; HCl ; FeCl_3 . These crystals were formed, however, in strongly undercooled solutions which contained from 8 to 25% of the solute. In solutions of greater dilution ordinary ice crystals were always obtained no matter how much the solution was undercooled. These crystals are described by Hartmann as follows:

- a. A mixture of right-angled and six-sided crystal skeletons. The six-sided plates are very similar to the ordinary snow stars with six rays. In the right-angled plates the individual crystal needles cut each other at an angle of 60° .
- b. Opaque spherulites, in which no radial structure could be observed because of the opacity.
- c. Opaque, spherical structure, built of opaque plates.
- d. Ice "feathers."

A series of experiments were carried out by Hartmann in which undercooled water was inoculated with ice crystals of form *a*, and the linear V. C. for the formation of crystals of this form determined. The results obtained were within the error of experiment the same as those obtained for the V. C. of ordinary ice crystals (form *d*). These experiments show, that even if the crystals that separated from the undercooled aqueous solutions are different from those formed in pure undercooled water, the V. C. is the same, consequently the retardation is not to be explained by the change in the form of the crystals.

Retarding Effect of Certain Colloids and Dissolved Gases.—Mention of an ester to a greater extent than salts with no water of crystallization." It is believed that the great effect of these salts is due to the fact that they are hydrated in solution. The assumption that the inorganic salts with water of crystallization form hydrates in solution would explain the abnormal behavior of FeCl_3 , CuCl_2 , CaCl_2 , etc., in this investigation. The formation of a hydrate would mean the existence of a molecular aggregate with a larger number of atoms. Since the retarding effect increases with the number of atoms in the molecule, the slowing down of the V. C. would be greater than would be expected from the formula of the anhydrous substance.

¹ *Z. anorg. Chem.*, 88, 128 (1914).

has already been made of the fact that it was impossible to determine the V. C. of gelatin and sodium oleate solutions at -9° because of spontaneous crystallization. The behavior of solutions containing these two substances was, however, much different from that of the majority of solutions that crystallize spontaneously. In the case of water or magnesium sulfate the crystals suddenly appear at one point in the tube and grow until the tube is filled. With the gelatin and the soap solution from five to seven nuclei develop at different parts of the tube at the same instant. Whether these substances have the power of increasing the number of crystallizing centers or merely develop latent centers, is a question that can be answered only by further experiment.¹ Experiments were also carried out with gelatin at -7.1° , at which temperature the tendency to crystallize spontaneously was not observed. The results obtained are given in Table IV. The retardation is doubtless due in part to such factors as the increase in the viscosity, also the change in thermal conductivity.

TABLE IV.

The velocity of crystallization of undercooled gelatin solutions. Temperature -7.1° .

Concentration.	Time per meter. Seconds.	Velocity cm. per minute.
Water.....	32.2	186
15.00 g. per liter.....	94.7	63.3
7.50 g. per liter.....	48.6	123'
3.75 g. per liter.....	43.2	139

The retardations of the V. C. by several other substances are given in Table V. Concentrated solutions of the dyes could not be used because the depth of color made it impossible to follow the progress of the crystallizing surface. The concentration of the dyes used was so low that little

TABLE V.

The influence of miscellaneous substances on the velocity of crystallization of water. Temperature -9.1° .

Compound.	Concentration.	Time per meter in seconds.	Velocity cm. per minute.
Wasser blau.....	1 g. in 5 l.	13.6	441
Safranin.....	1 g. in 0.5 l.	16.8	357
Malachite green.....	1 g. in 2.0 l.	17.4	345
Säure violet.....	1 g. in 2.5 l.	15.1	397
Methylene blue.....	1 g. in 5.0 l.	19.7	304
Rosaniline.....	Satd. soln. at room temp.	18.0	333
Carbon dioxide.....	Satd. soln.	17.2	348
Oxygen.....	Satd. soln.	18.6	323
Ferric hydroxide colloidal soln..	Concentrated	34.1	176

can be learned concerning their effects. In general, they stabilize the undercooled solution greatly, spontaneous crystallization occurring much less frequently than with the substances in Table II. Of particular

¹ "Kristallisieren und Schmelzen," p. 148.

interest is the fact that the solutions containing dissolved carbon dioxide and oxygen could be readily undercooled and were fairly stable towards

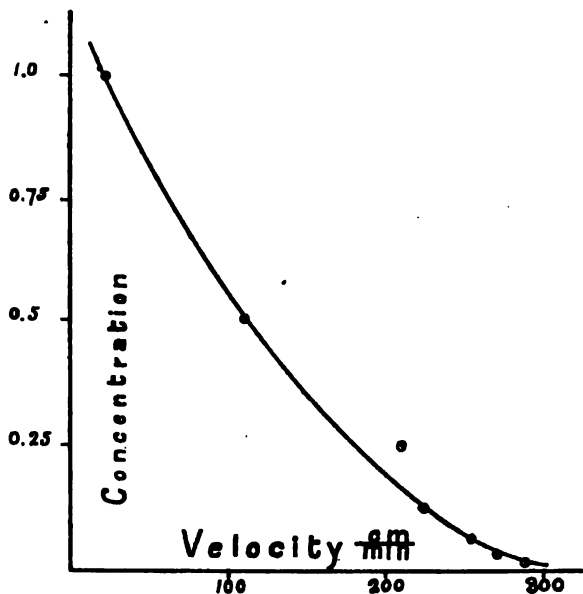


Fig. 2.

spontaneous crystallization. This seems to disprove the often repeated statement that gas-free water is absolutely necessary to successful undercooling.

Further experiments were carried out in which there was measured (1) the V. C. of 0.1 *M* hydrochloric acid solutions from -4° to -10° , (2) the V. C. of undercooled solutions of hydrochloric acid of different concentrations. The results are given in Tables VI and VII and are shown graphically

in Figs. 1 and 2. Table VIII (Fig. 3), gives the results obtained with solutions of brucine sulfate of various concentrations at -9.1° .

TABLE VI.

The velocity of crystallization of undercooled aqueous solutions of 0.1 *M* hydrochloric acid at various temperatures.

Temperature.....	-4.1°	-5.1°	-6.1°	-7.1°	-8.1°	-9.1°	-10.1°	-10.7°
Velocity cm. per minute.....	75.0	113.0	144.0	178.0	223.0	249.0	280.0	309.0

TABLE VII.

The velocity of crystallization of undercooled aqueous solutions of hydrochloric acid of various concentrations. Temperature -9.1° .

Concentration gram mols per liter.....	1.0	0.5	0.25	0.125	0.0625	0.03125	0.01563
Velocity cm. per min.....	21.3	109.0	211.0	226.0	258.0	271.0	291.0

TABLE VIII.

The velocity of crystallization of undercooled aqueous solutions of brucine sulfate of various concentrations. Temperature -9.1° .

Concentration gram mols per liter.....	0.02	0.01	0.005	0.0025	0.00125	0.000625
Velocity cm. per minute.....	114.0	154.0	236.0	309.0	365.0	365.0

In this series of experiments it was found that although brucine sulfate when present to the extent of 0.00125 and 0.000625 gram mol per liter had no effect on the V. C. of the solvent; it did have a remarkable effect in preventing spontaneous crystallization, for solutions of this concentration can be easily undercooled and are much more stable than pure water.

Summary.

The results of this investigation may be briefly summarized as follows:

1. The velocity of crystallization of ice from aqueous solutions of 45 substances has been determined at -9.1° . The dissolved substances all retard the

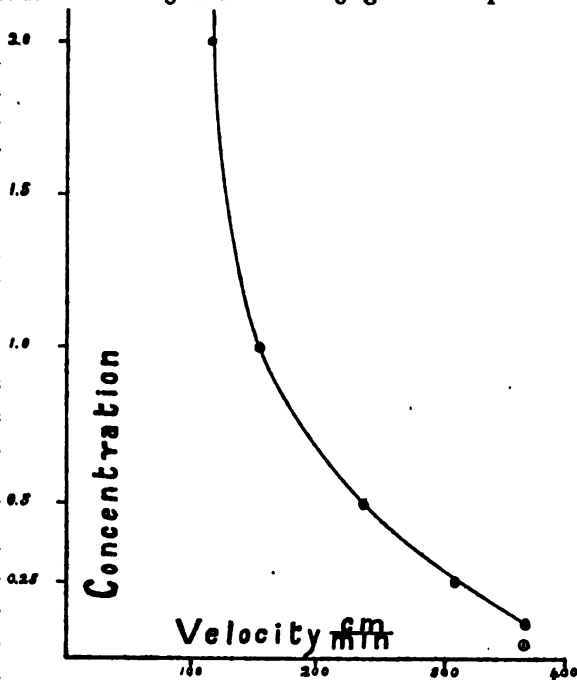


Fig. 3.

velocity of crystallization. In no case has an acceleration been observed.

2. Solutions of equimolecular concentrations show different retarding effects. The retardation is not, therefore, a colligative property.

3. For substances with more than 8 atoms in the molecule there is a rough relation between the number of atoms in the molecule and the inhibition of the velocity of crystallization; the greater the number of atoms, the lower the rate. For compounds with less than 8 atoms, the power of retardation seems to be a specific property.

4. That these effects cannot be explained by Marc's adsorption theory of the inhibition of crystallization is evidenced by the fact that the sugars, which are not greatly adsorbed, are very active in retarding the rate of crystallization. Certain inorganic salts also show no relation between the extent to which they are adsorbed, and their retardation of the formation of ice crystals.

5. Substances in the colloidal state such as gelatin, ferric hydroxide and certain dyes retard the velocity of crystallization.

6. The stability of the undercooled solutions towards spontaneous crystallization varies with the solute. 0.1 M solutions of hydrochloric acid are exceptionally stable.

Dilute solutions of certain dyes are also unusually stable. Solutions of brucine sulfate with a concentration less than 0.00125 gram mol per liter do not affect the velocity of crystallization. These solutions, however, are much more stable toward spontaneous crystallization than pure water at the same temperature.

MADISON, WISCONSIN.

DIFFERENTIAL IODIMETRY.

1—DETERMINATION OF PERIODATES, IODATES, BROMATES AND CHLORATES IN THE PRESENCE OF EACH OTHER.*

By O. L. BARNEBY.

Received December 2, 1915.

Considerable work has been done by various investigators¹⁻²⁵ who have studied the rates of reaction between oxidizing agents of the type of the oxidized halogen compounds and potassium iodide. The larger portion of the previous work has been from a physico-chemical viewpoint, performed in an endeavor to establish the order of these reactions. This study has for its purpose the investigation of such reactions to ascertain the conditions under which they are applicable to analytical chemistry.

When potassium iodide is added to oxidizing agents in acid solution, free iodine is liberated more or less completely, the quantity of oxidizing agent transposed depending upon the concentrations of the substances involved, the temperature, and to a certain extent the pressure. The greater the concentration of iodide the more rapid the reaction. The greater the dissociation of the acid as well as the larger the amount of acid involved the faster the liberation of iodine occurs. This principle has been utilized for the purpose of determining the strength of acids²⁶⁻³⁶, a mixture of iodide and iodate having been utilized for the purpose.

The utilization of such reactions for direct quantitative purposes has been studied to a comparatively limited extent. Certain reactions, like those between cupric salts, ferric salts, permanganate, dichromate, and the halogenates and an iodide, have been shown to be quantitative for the individual reactions, and they form the basis of laboratory determinations in common use. Moser⁴⁴ converted iron into a complex by the use of pyrophosphoric acid and titrated copper in the presence of iron. Edgar⁴⁵ reduced chromic and vanadic acids with hydrobromic acid, distilling into potassium iodide, then reduced the vanadium and iron with hydriodic acid, again distilling. In each case the iodine was titrated with thiosulfate. An arsenite method was used for the determination of chromic acid. By combining the schemes, chromic acid, vanadic acid and ferric iron were determined. However, no systematic study has

* Presented at the Seattle meeting of the American Chemical Society, August 30th to September 4th.

been made in which it was attempted to titrate various oxidizing substances in the presence of each other, utilizing varying concentrations of acid and iodide to liberate iodine in a differential manner, subsequently titrating the iodine with a reducing agent such as thiosulfate. This paper considers the determination of periodates, iodates, bromates and chlorates in the presence of each other and also in the presence of perchlorates.

The halogenate solutions used in this investigation were tenth normal. The sodium thiosulfate and sodium arsenite solutions were approximately tenth normal and were accurately standardized when used. The potassium iodide solution was normal and contained no liberated iodine.

Determination of Periodate in the Presence of Iodate, Bromate and Chlorate.

Müller and Friedberger⁴⁶ state that periodate can be titrated in the presence of iodate, using an acidity of acetic acid between the concentrations of 0.02 *N* and 0.1 *N* with thirty per cent. sodium acetate. No results are recorded. However, they further state that an arsenite method, which is described, surpasses the thiosulfate method in exactness.

Periodates in neutral solution react with potassium iodide, yielding iodate and free iodine. The free iodine can be accurately titrated in the presence of an excess of sodium bicarbonate with a standard arsenite solution prepared in the usual manner. This confirms the work of Müller and Friedberger.

If an attempt is made to titrate the free iodine with thiosulfate, erratic results are obtained. If a weak acid is added to remove the alkali formed, conditions are improved somewhat; however, great care must be exercised in the choice of the acid and the concentration of the same. The acid must be very weak, otherwise it will cause interaction of iodide and iodate. The use of acetic acid and sodium acetate mentioned by Müller and Friedberger was found to be unsatisfactory. Stearic acid and sodium stearate, palmitic acid and sodium palmitate, carbonic acid and sodium bicarbonate were tried, but satisfactory results were not obtained.

When boric acid and an iodide are added to a solution containing a periodate, the latter is converted to iodate and the liberated iodine can be titrated with thiosulfate. However, the iodate is affected slightly. This slight effect can be removed by the addition of borax (normal sodium borate also has the same effect) which diminishes the acidity of the boric acid to a sufficient extent to practically prevent the iodate reaction. (Table I.)

The titrations were performed at room temperature. The results show that addition of solid boric acid in excess and two grams of borax to the iodate solution gives such a very slight reaction between 0.1 *N* iodide and a 0.1 g. of iodate in a volume of 100 cc., and that the iodate influence may be

considered negligible during the titration of the iodine resulting from the periodate decomposition.

TABLE I.—INFLUENCE OF BORIC ACID AND BORAX UPON THE REACTION BETWEEN IODATE AND IODIDE.
Volume 100 cc.

Expt. No.	Boric acid. G.	Borax. G.	Time. Hours.	KIO ₃ present. G.	KIO ₃ indicated. G.	Oxygen. indicated. G.
1.....	2	0.1	24	0.0892	0.0138	0.00096
2.....	2	0.2	24	0.0892	0.0048	0.00034
3.....	2	0.5	24	0.0892	0.00071	0.00005
4.....	2	1.0	24	0.0892	0.00021	0.00002
5.....	2	2.0	24	0.0892
6.....	2	4.0	24	0.0892
7.....	2	6.0	24	0.0892
8.....	4	...	24	0.0357	0.0437	0.00304
9.....	2	...	24	0.0892	0.0564	0.00355
10.....	solid in excess	2	24	0.0892	0.0003	0.00002

Allowing thiosulfate in excess to remain a short time in the presence of iodate does not cause reduction of iodate. However, periodate does react with thiosulfate, hence the periodate should be allowed to react completely with iodide before titration is commenced, otherwise, results may be vitiated to a greater or less extent. Three minutes is sufficient time to allow for the completion of the periodate reaction.

TABLE II.—DETERMINATION OF PERIODATE BY REACTION WITH IODIDE IN SOLUTIONS CONTAINING BORIC ACID AND BORAX.

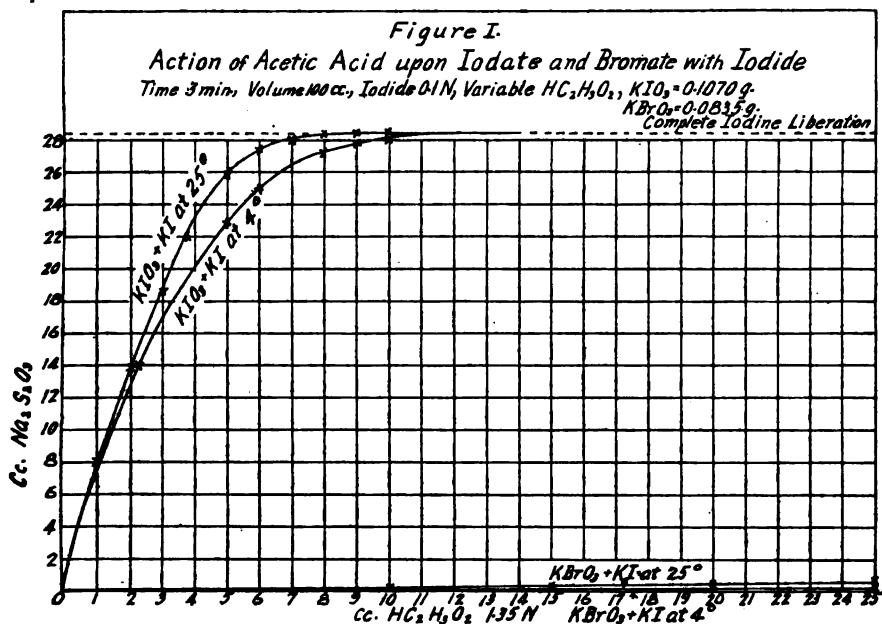
Experiment No.	Added.		KIO ₃ .	
	Substance.	Gram.	Present. G.	Found. G.
1.....	0.2835	0.2839
2.....	0.2835	0.2836
3.....	0.1134	0.1135
4.....	0.0567	0.0568
5.....	0.5670	0.5669
6.....	KIO ₃	0.0892	0.0567	0.0568
7.....	KIO ₃	0.0892	0.1134	0.1137
8.....	KIO ₃	0.0892	0.2835	0.2836
9.....	KBrO ₃	0.1	0.1134	0.1135
10.....	KClO ₃	0.1	0.1134	0.1132
11.....	KClO ₄	0.1	0.1134	0.1136

A series of periodate titration results is given in Table II. In each experiment 2 g. of borax were added to the solution (about 90 cc.) containing the periodate in an Erlenmeyer flask, followed by an excess of solid boric acid and 10 cc. of normal potassium iodide. The total volume was 100 cc. in each instance. Three minutes' time was allowed for interaction of iodide and periodate, after which the resulting iodine was titrated with standard thiosulfate to the disappearance of the iodine color. The column "g. KIO₃ present" contains the amounts of periodate com-

puted on the basis of the sodium arsenite titration in bicarbonate solution. The results of the two methods are thus seen to be in close agreement. Bromate, chlorate, perchlorate, as well as iodate, do not interfere.

Determination of Iodate in Presence of Bromate and Chlorate.

For the liberation of iodine from an iodide by iodate only a slight acidity of a mineral acid is required; however, bromate also reacts with iodide in only slightly acid solutions when mineral acids are used. With acetic acid there is a marked difference between iodate and bromate within certain limits of acidity (see Fig. 1). At room temperature (25°) it was found that 0.125 *N* acetic acid in presence of 0.1 *N* iodide would cause liberation of iodine corresponding to the entire oxidizing value of



0.1 g. of iodate in a volume of 100 cc. within three minutes. On the other hand 0.1 g. of bromate under the same conditions liberated a slight amount of iodine, sufficient to require 0.30 cc. of 0.1 *N* thiosulfate when the reaction had proceeded for three minutes. This bromate reaction can be retarded by the addition of sodium acetate, but when a sufficient amount is added to accomplish the purpose the speed of the iodate reaction is also lessened, requiring a much longer time for its reaction with the iodide and the lengthened time introduces the bromate influence again. The extent of the action of the bromate is appreciably lessened by lowering the temperature, the iodate being much less affected thereby. A very effective method found to be applicable was to chill to 3° or 4° the solu-

tion containing 0.25 *N* acetic acid and 0.1 *N* iodide, under which conditions 0.1 g. of potassium bromate in 100 cc. required 0.15 cc. of 0.1 *N* thiosulfate for titration of the iodine liberated at the end of three minutes. For smaller amounts of bromate a correspondingly smaller quantity of thiosulfate is required (see Table III).

TABLE III.—DETERMINATION OF IODATE IN PRESENCE OF BROMATE.

Experiment No.	KBrO ₃ present. G.	Na ₂ S ₂ O ₄ .			KIO ₃	
		Total cc.	Blank cc.	Corrected cc.	present. G.	found. G.
1.....	0.0835	9.48	0.08	9.40	0.0357	0.0357
2.....	0.0557	9.44	0.04	9.40	0.0357	0.0357
3.....	0.0413	18.84	0.00	18.84	0.0714	0.0715
4.....	0.0278	28.24	0.02	28.22	0.1070	0.1070
5.....	0.0835	4.74	0.06	4.68	0.0178	0.0177
6.....	0.0835	1.04	0.10	0.94	0.0036	0.0036
7.....	0.0974	28.40	0.14	28.26	0.1070	0.1071
8.....	0.1531	28.48	0.18	28.30	0.1070	0.1073
9.....	0.1531	1.12	0.18	0.94	0.0036	0.0036

The procedure adopted for the determination of iodate in presence of bromate is as follows: A 0.1 g. sample* (or corresponding aliquot portion if in solution) is dissolved in about seventy cc. of water in an Erlenmeyer flask and the solution chilled in ice water for some time. To the cooled solution is added about 10 cc. of normal potassium iodide, followed by about 20 cc. of 1.25 *N* acetic acid also chilled in ice water. The time is noted and the solution allowed to stand a minute or more; then the titration with standard thiosulfate is completed at the end of a certain definite time—let us say three minutes (not less). The titration is conducted with the solution immersed in a dish of water containing an excess of ice. After the titration has been completed and the reading noted the solution is allowed to stand in ice water an equal length of time and more thiosulfate is again added to bleach any iodine which may have been produced by action of bromate. The second titration is the amount of thiosulfate which must be subtracted from the first titration, inasmuch as it represents the amount of bromate decomposed during the titration of the iodate. On the basis of the corrected volume of thiosulfate the iodate is computed. The results of Table III show that excellent results can be obtained in the presence of relatively small and large amounts of bromate, the only effect of the varying quantities of bromate being to vary the amount of the "blank" to be subtracted from the total volume of thiosulfate required in the first titration. Naturally, any periodate present with the iodate would be titrated by this procedure, thus giving a means of determining their total oxidizing value, and by application of the pre-

* In some experiments of Table III larger amounts of bromate are used than corresponds to this weight of sample, the purpose being to show in more marked manner the effect of the bromate.

ceding titration of periodate in the presence of iodate the two can be determined in the presence of each other.

Determination of Bromate in Presence of Chlorate.

Bromate will liberate iodine from an iodide with much lower acidity than will chlorate; however, weak acids will not cause iodide to completely transpose the bromate within a reasonable period of time. A preliminary study of the effect of various acids and potassium iodide upon chlorate and bromate indicated dilute hydrochloric acid to be very well adapted for the determination of the bromate without chlorate interference (Fig. 2).

Table IV contains the results of determinations of bromate under various conditions. In all cases the temperature was that of the room (24°) except in Expt. 14, in which case the solutions were chilled in ice water to about 4°. The solutions were prepared by adding the acid after all the other reagents. Expts. 6-12 show a wide latitude in the amount of acid which may be added without introducing an appreciable error due to chlorate. Expts. 1-5 and 15-17 show that 0.1 g. of potassium bromate may be accurately titrated in 100 cc. of a solution which contains 0.05 *N* iodide and 0.2 *N* hydrochloric acid within a reasonable time after adding the various reagents.

TABLE IV.—DETERMINATION OF BROMATE IN THE PRESENCE OF CHLORATE.

Total volume in each experiment = 100 cc.

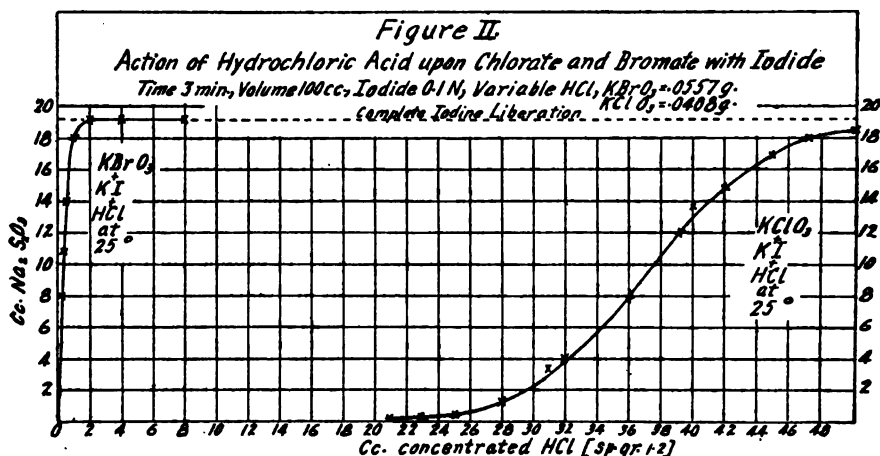
Experiment No.	KI. Normality.	HCl ^{6N} sp. gr. l.l. cc.	Time. Min.	KClO ₃ present. G.	KBrO ₃	
					present. G.	found. G.
1.....	0.05	2	1	..	0.0557	0.0474
	2	0.0505
	3	0.0513
2.....	0.05	3	1	..	0.0557	0.0550
	2	0.0559
3.....	0.05	5	Immediate	..	0.0557	0.0557
4.....	0.05	5	Immediate	..	0.1114	0.1114
5.....	0.05	5	Immediate	..	0.1392	0.1393
6.....	0.05	5	3	0.1021	..	0.0001*
7.....	0.05	10	3	0.1021	..	0.0001*
8.....	0.05	10	32	0.1021	..	0.0002*
9.....	0.05	20	3	0.1021	..	0.0002*
10.....	0.05	20	26	0.1021	..	0.0008*
11.....	0.05	25	3	0.1021	..	0.0002*
12.....	0.05	30	3	0.1021	..	0.0003*
13.....	0.05	45	3	0.1021	..	0.0029*
14.....	0.05	45	3	0.1021	(at 4°)	0.0001*
15.....	0.05	5	Immediate	0.1021	0.0557	0.0556*
16.....	0.05	5	Immediate	0.1021	0.1392	0.1393*
17.....	0.05	5	Immediate	0.1021	0.1114	0.1114*

* A slight trace of bromate was present in the chlorate used, which accounts for the slight liberation of iodine immediately and no more liberation for a considerable period of time in experiments 6-9, 11 and 12.

Should periodate or iodate be present they will give up their available oxygen to potassium iodide for iodine liberation and hence be titrated also. By use of the previously outlined methods the periodate, iodate and bromate may be determined in presence of each other.

Determination of Chlorate in the Presence of Perchlorate.

Perchlorate⁴⁷ will not readily liberate iodine from potassium iodide in acid solution at ordinary temperatures. Although chlorate has an inappreciable rate of reaction with iodide in dilute acid solution, when the acid concentration becomes considerably stronger the rate increases with increasing acidity very markedly, until the chlorate can be completely transposed with an equivalent liberation of iodine (Fig. 2).



As is well known, considerable care must be exercised when high concentrations of acid and iodide are involved to prevent the air from causing high results. The oxygen of the air, either directly or through the intermediate formation of ozone, liberates iodine quite readily from such solutions. If the temperature is increased the rate is much accelerated. Moreover iodine cannot be accurately titrated with thiosulfate in strong acid solutions, inasmuch as the latter decomposes the thiosulfate during titration. Hence the air in the flask must be replaced by an inert atmosphere, such as carbon dioxide, before starting the experiment. Likewise, the large excess of acid must be removed by neutralization or dilution before titration.

Various so-called "Inducing Agents"⁴⁷⁻⁴⁸ were tried to increase the rate of reaction of chlorate and iodide at a low acid concentration, but they were not found to be as serviceable as was anticipated. Arsenious acid, cuprous chloride, manganous chloride, cerous chloride and thallous chloride produced practically no effect. Vanadyl salts and ferrous salts ac-

celerated the reaction, but not to a sufficient extent to warrant their use for this purpose. The application of vanadium would introduce a colored solution which would also be a disadvantage. While the vanadium and iron salts increased the rate, it was difficult to make the last trace of chlorate react by the use of low acid concentration with these "inducers" present.

A method of treating the chlorate to form an equivalent amount of iodate and then titrating the iodate gives excellent results. This conversion is accomplished by liberating iodine by the reaction of the chlorate with iodide in strong acid solution and then dissolving the iodine by addition of alkali. After cooling the solution, it is made faintly acid with hydrochloric acid which causes reaction between iodate and iodide, and the iodine is then titrated with thiosulfate.

TABLE V.—DETERMINATION OF CHLORATE IN PRESENCE OF PERCHLORATE.

Experiment No.	HCl normality.	KI normality.	Total volume. cc.	Time. Min.	KClO ₄ present. G.	KClO ₃	
						present. G.	found. G.
1.....	2.7	0.10	100	3	..	0.0408	0.0008
2.....	2.7	0.10	100	6	..	0.0408	0.0015
3.....	2.7	0.10	100	15	..	0.0408	0.0032
4.....	4.1	0.10	100	3	..	0.0408	0.0039
5.....	4.1	0.10	100	6	..	0.0408	0.0076
6.....	5.4	0.10	100	3	..	0.0408	0.0340
7.....	5.4	0.10	100	6	..	0.0408	0.0373
8.....	5.4	0.10	100	15	..	0.0408	0.0404
9.....	5.4	0.20	100	3	..	0.0408	0.0347
10.....	5.4	0.20	100	6	..	0.0408	0.0378
11.....	5.4	0.20	100	15	..	0.0408	0.0408
12.....	6.7	0.20	100	3	..	0.0408	0.0402
13.....	6.7	0.20	100	6	..	0.0408	0.0405
14.....	6.7	0.20	100	15	..	0.0408	0.0408
15.....	6.7	0.20	100	5	..	0.0612	0.0609
16.....	6.7	0.20	100	15	..	0.0612	0.0611
17.....	5.6	0.16	120	5	..	0.1021	0.0980
18.....	5.6	0.16	120	10	..	0.1021	0.1011
19.....	5.6	0.16	120	12	..	0.1021	0.1022
20.....	5.6	0.16	120	15	..	0.1021	0.1021
21.....	5.6	0.16	120	21	..	0.1021	0.1021
22.....	6.0	0.20	100	15	0.1000	0.1021	0.1023
23.....	6.0	0.20	100	15	0.2000	0.1021	0.1022
24.....	6.0	0.20	100	15	0.5000	0.1021	0.1024
25.....	6.0	0.20	100	15	0.5000	..	0.0001

Table V contains a series of titration results with and without perchlorate present. In these experiments a 500 cc. glass-stoppered flask or bottle was used. Carbon dioxide was passed into the bottle or flask to remove the air, then the solutions were introduced in the amounts enumerated in the table. The flask or bottle was kept stoppered during the decomposition period. After lapse of the time specified the stopper,

was removed, a watch glass or inverted crystallizing dish substituted and a slight excess of sodium hydroxide was added all at once and the solution shaken immediately, meantime cooling it in running water. 100 cc. of water were then added to wash down the sides of the vessel and to dilute the solution. The amount of sodium hydroxide was regulated by using a solution of such strength that each cubic centimeter neutralized one cubic centimeter of acid originally added. The use of a calculated amount makes it possible to add a slight excess of alkali at once, without danger of adding an insufficient amount, in which latter case iodine would be volatilized by the heat of reaction between the strong acid and alkali. The solution was cooled to room temperature, then hydrochloric acid (6 *N*) was added slowly with agitation of the solution until free iodine was liberated in quantity, followed by about 3 cc. more. The iodine was then titrated with thiosulfate.

The results given in Table V show that chlorate can be titrated iodimetrically without distillation. By the use of a pressure bottle and heating the solution the time of reaction and also the concentration of reagents could undoubtedly be reduced, but such a procedure would greatly increase the tendency for any slight amount of oxygen present in the bottle to react with the hydriodic acid, inasmuch as hot hydriodic acid readily reacts with the oxygen of the air. Experiments 9-21 show that 6 *N* hydrochloric acid and 0.2 *N* potassium iodide in a volume of 100 cc. will cause complete transposition of 0.1 g. of chlorate within a period of fifteen minutes at room temperature (21°). Experiments 6-11 indicate only a slight advantage of 0.2 *N* over 0.1 *N* iodide. Experiments 21-25 show that chlorate can be accurately titrated in the presence of perchlorate under the conditions outlined.

Periodate, iodate and bromate are also transposed by iodide in strong acid solutions, hence they would be titrated with chlorate in such solutions. In such cases the periodate, iodate and bromate should be titrated separately and the amount of chlorate ascertained by difference.

Analysis of Mixtures containing Periodate, Iodate, Bromate, Chlorate and Perchlorate.

Separate 0.1 g. samples are taken for each titration, for all except the periodate, in which case 0.2-0.3 g. samples are used, or a 2 g. sample is dissolved and diluted to a liter and 50-cc. portions (100 cc. in case of periodate) of the larger sample are used for the individual titrations.

Periodate.—The 0.2 g. sample in 100 cc. volume is treated in a suitable Erlenmeyer flask with 2 g. of borax, an excess of solid boric acid and 20 cc. of normal potassium iodide added, and the solution allowed to stand three minutes. The iodine is then titrated with standard sodium thiosulfate (about 0.1 *N*). Or, to the sample may be added sodium bicarbonate

in excess, followed by 10 cc. of normal potassium iodide and titration of the iodine with standard arsenite solution.

Periodate and Iodate.—A 0.1 g. sample in 70 cc. of solution is chilled in ice water to about 3° or 4° and to the chilled solution is added 10 cc. of normal potassium iodide and 20 cc. of one-fourth normal acetic acid, also chilled in ice water. After standing a minute or two the thiosulfate titration is started and completed within a definite time from the moment of addition of acid and iodide (let us say three minutes, not less). The solution is then allowed to stand an equal time longer and any iodine which appears again titrated with thiosulfate. This second reading is subtracted from the first to give the corrected volume of thiosulfate equivalent to periodate and iodate.

Periodate, Iodate and Bromate.—To a 0.1 g. sample in a volume of about 90 cc. is added 10 cc. of normal potassium iodide and 5 cc. of six normal hydrochloric acid and the free iodine titrated with thiosulfate.

Periodate, Iodate, Bromate and Chlorate.—A 0.1 g. sample is dissolved in 50 cc. of water contained in a 500 cc. glass-stoppered bottle or flask and carbon dioxide passed into the vessel to effect as complete elimination of air as possible. 10–20 cc. of normal potassium iodide and 50 cc. of hydrochloric acid (sp. gr. 1.2) are added and the solution is allowed to stand 20 minutes. The stopper is then replaced by a watch glass or inverted small crystallizing dish, and while the solution is being cooled in running water, 50 cc. of sodium hydroxide solution (550 g. of 95% NaOH per liter of solution) are added *all at once* and the solution is twirled immediately.* After cooling the solution to room temperature 100 cc. of water are added to wash down the sides of the bottle or flask and for dilution. Six normal hydrochloric acid is then added slowly until iodine is liberated in quantity, followed by 3–5 cc. more of the acid. The free iodine is then titrated with the thiosulfate.

Perchlorate does not react readily with potassium iodide in acid solutions at ordinary temperatures and consequently cannot be determined in this manner.

The amount of thiosulfate required for each compound present is found by subtraction from each collective titration, the amount of thiosulfate, computed on the basis of equivalent samples, required for the next preceding groups titrated.

In the analysis of the mixtures given in Table VI the periodate, iodate, bromate, chlorate and perchlorate were weighed out accurately, transferred to a 250 cc. volumetric flask, dissolved in water and diluted to the mark. The potassium periodate contained iodate, hence the iodate con-

* The solution at this point should be colorless, all the iodine being converted to iodate. If not colorless the heat of reaction will volatilize some iodine and cause low results, showing the addition of an insufficient amount of hydroxide.

tent of the periodate (as ascertained by previous analysis) weighed for each mixture, was added to the weight of iodate to get the actual iodate involved. Likewise the weight of periodate given is based upon the analysis. Aliquot portions were titrated by the method given previously and the weight of each compound of the mixture was computed. The perchlorate was calculated by difference.

TABLE VI.—ANALYSIS OF HALOGENATE MIXTURES.

	KIO ₄		KIO ₃		KBrO ₃		KClO ₃		KClO ₄	
	present. G.	found. G.	present. G.	found. G.	present. G.	found. G.	present. G.	found. G.	present. G.	found. G.
Mixture I	0.2268	0.2268	0.2112	0.2110	0.0557	0.0562	0.0409	0.0410	0.1000	0.0998
Mixture II	0.1134	0.1136	0.3732	0.3728	0.0557	0.0561	0.0409	0.0406	0.1000	0.1001
Mixture III	0.0567	0.0565	0.0974	0.0974	0.2228	0.2231	0.0409	0.0405	0.1000	0.1003
Mixture IV	0.0567	0.0566	0.0974	0.0972	0.0557	0.0557	0.1636	0.1632	0.1000	0.1007
Mixture V	0.0567	0.568	0.0161	0.0162	0.2230	0.2230	0.0041	0.0040	0.1000	0.0997
Mixture VI	0.0057	0.0057	0.3576	0.3574	0.0056	0.0058	0.1636	0.1634	0.1000	0.1002

The results are thus seen to be good. The greatest error falls on the perchlorate, which has been determined entirely by difference. The perchlorate is introduced here mostly to show its negative effect on the other determinations, inasmuch as a method which relies entirely on calculation by difference is encumbered by many discrepancies and in general is not to be recommended. In a sense each titration, except the first one, involves a calculation by difference. However, the titration of the ingredient desired is a direct cumulative titration of the particular compound and on the basis of this increase its percentage or weight is computed. The result calculated from each titration is dependent only on that and the one next preceding. Periodates have a tendency to decompose with more or less ease, hence should be analyzed as soon as possible after weighing.

Summary.

1. Certain oxidizing agents can be determined in the presence of each other iodimetrically in a differential manner by regulation of the concentration of reagents, especially the acidity, the temperature and the time of reaction.
2. Periodate reacts completely with iodide in saturated boric acid solution, containing sufficient borax to diminish the acidity to a slight extent, forming iodate and free iodine.
3. Iodate is acted on by 0.1 N iodide in 0.25 N acetic acid solution and the free iodine can be titrated.
4. In 0.2 N hydrochloric acid solution containing 0.1 N iodide, bromate is completely decomposed, and the free iodine can be titrated.
5. 6 N hydrochloric acid acting in presence of 0.1–0.2 N iodide decomposes chlorate completely. After rendering the solution alkaline, and then acidifying the iodine can be titrated with thiosulfate.

6. By combination of 2, 3, 4 and 5, periodate, iodate, bromate and chlorate can be determined differentially in the presence of each other and in the presence of perchlorate.

The differential-deportment of other oxidizing agents will also be studied.

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THE ELECTROMETRIC TITRATION OF VANADIUM.

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The titration of chromates with ferrous sulfate, using as an end point the change in potential of a platinum electrode immersed in the solution

has been recently used by Hildebrand¹ and Forbes and Bartlett.² While working on the application of this method to the determination of chromium in steel, it was found that vanadium in the pentavalent condition may be titrated in a very similar manner. If both chromates and vanadates are present, the titration includes both elements. We, therefore, determined to test this as a possible new method for the determination of vanadium.

Volumetric methods for the determination of vanadium usually involve the titration of vanadyl salt with potassium permanganate. To a less extent the determination is made with ferrous sulfate, using potassium ferricyanide as either inside or outside indicator, more often the latter.

In the first class of methods, reduction is accomplished by hydrochloric acid, sulfur dioxide, hydrogen peroxide, oxalic acid, and other reducing agents. The chief objections which have been made to these methods are (1) that the state of oxidation of the vanadium after reduction is uncertain³ and (2) that the residual solution after reduction may not be entirely free from the reducing agent. The second class of methods is criticized by Cain⁴ as being faulty in that vanadyl salts reduce ferricyanide which then reacts with ferric salts, with the result that the values obtained are too low. Clark⁵ replies to this that well-washed ferricyanide crystals in fresh solution are not acted upon by vanadyl salts, and that the result is correct. Bleecker⁶ states that vanadyl salts added to ferric salts immediately reduce a part to the ferrous condition. One of us (Kelley) in trying Clark's method, which involves reduction with ferrous sulfate and back titration with potassium dichromate, using potassium ferricyanide as an outside indicator, found it to give variable and high results. This seems to be contrary to the experience of Cain and Bleecker as well as Clark. The tendency of Clark's method to give high results has been shown again in this investigation, for the addition of appreciable amounts of ferrous sulfate solution was found necessary to obtain the end point of Clark's method after our own end point had been reached. We take occasion to mention these points concerning the reduction of vanadates with ferrous sulfate because our method depends upon this, although it differs from other methods in the manner of obtaining the end point. In the experimental portion of the paper, we show results obtained by several methods and compare them with our own.

¹ THIS JOURNAL, 35, 869 (1913).

² *Ibid.*, 35, 1527 (1913).

³ Auchy, *J. Ind. Eng. Chem.*, 1, 455 (1909).

⁴ *Ibid.*, 3, 477 (1911).

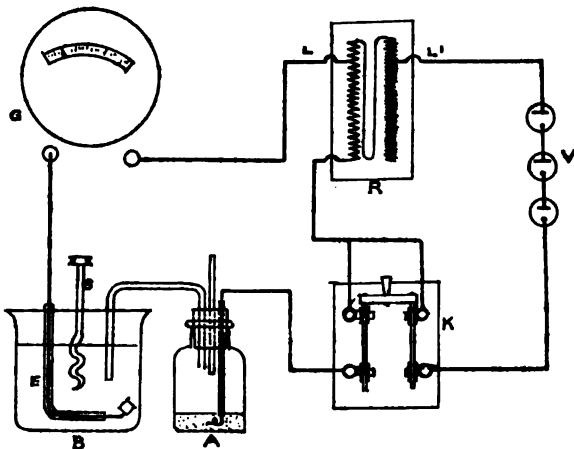
⁵ *Met. Chem. Eng.*, 11, 195-7.

⁶ *Ibid.*, 9, 209 (1911).

Apparatus.

Since the aim of the investigation was the analytical determination of vanadium no attempt was made to measure the actual potentials involved. It was required only that the apparatus be of such a nature that we could readily detect the sudden changes of potential which corresponded to the disappearance of the higher state of oxidation of the element in question. This enabled us to replace the reflecting galvanometer which Forbes and Bartlett used with an ordinary suspension galvanometer, and the slide-wire bridge with a resistance box containing two sliding contacts. The latter change was possible because we made no readings of the resistances involved, the changes of position of the galvanometer needle alone being noted. The resistance box, which consisted of two coils and sliding contacts with resistances of 195 and 5 ohms, was wired so that one resistance served to vary the e. m. f. of the dry cells used as the source of current and the other served as the potentiometer box.

In the diagram of our apparatus, A represents a calomel electrode conveniently made from a small wide-mouth bottle filled with a solution of KNO_3 . The dotted area in A indicates the portion of bottle occupied by the mercury. It is provided with a plunger, slight pressure on which causes the ejection of a portion of the liquid through a capillary tube. B represents the beaker in which the titration is made and containing the platinum electrode E and the stirrer S. The galvanometer is shown at G and the resistance box at R, with its two sliding contacts L and L'. The batteries, ordinary dry cells, are shown at V, and K is a double knife switch which throws in both the galvanometer and main circuits at one operation.



The Titration of a Solution.

The solution containing the unknown amount of vanadium as vanadate is placed in the beaker and 25 cc. of H_2SO_4 (sp. gr. 1.4) are added with water enough to bring the volume up to 200 cc. The connections are then made and resistances so adjusted that the needle comes to rest on the scale. Standard ferrous sulfate solution is then run in from the buret. At the first addition of ferrous sulfate the needle begins to move off of the

scale, showing a drop in potential. The sliders on the resistance box are then changed in such a manner as to keep the needle on the scale during the addition of further quantities of the reducing agent. This movement of the needle is slow and continues until one-half to three-fourths of the equivalent quantity of ferrous sulfate solution has been added. During the addition of the last quarter the needle remains practically at rest until the end point is reached, when the addition of a few tenths of a cubic centimeter in excess causes a sudden movement. To obtain exact adjustment, dilute standard dichromate solution is added in small amount until the needle is returned to the position which it occupied before ferrous sulfate was added in excess. The addition of two or three drops of the ferrous sulfate solution is now usually enough to cause a sudden movement over several divisions. This is followed by the addition of exactly the quantity of dichromate necessary to return the needle to the original stationary position. The end point in the reaction is thus indicated by a sharp throw of the needle which is easily distinguished from the slow movement which occurs when the first portions of ferrous sulfate are added. The final adjustment to get the exact end point will rarely require the addition of more than 0.5 cc. of standard dichromate solution, for, even if the addition of ferrous sulfate has been rapid, the end point will not usually be passed by more than this amount. However, this titration is much more sensitive to conditions than is the titration of chromates. Accordingly, we give below a few of our experiments which show favorable and unfavorable conditions for the titration.

Conditions for Titrating Vanadates.

The object of these experiments was to find the conditions which gave the maximum throw of the needle for a given excess of ferrous sulfate, that is, the sharpest end point. To this end varying amounts of pure ammonium vanadate solution were titrated with ferrous sulfate and potassium dichromate as described above under conditions differing as to temperature, and concentration of foreign salts and acid. Solutions having a volume of 250 cc. of the composition given in Table I were titrated to within a few drops of the end point. The resistance was then adjusted until the needle came to rest at zero on the galvanometer. Record was then made of the deflection following the addition of each drop of ferrous sulfate. In this way a rough but serviceable idea could be obtained of the sharpness of the end point under the given conditions. After the addition of these several drops of ferrous sulfate, enough dichromate was added to bring the needle back to the position which it occupied before the first deflection caused by the addition of ferrous sulfate. From the buret readings the vanadium content was calculated for comparison with the known weight in the solutions taken.

TABLE I.—EFFECT OF CONDITIONS UPON END POINT.

Temp. ° C.	H ₂ SO ₄ Sp. gr. 1.40. cc.	Additions.	Change in reading of gal- vanometer with successive drops of ferrous sulfate.							Vanadium	
			1.	2.	3.	4.	5.	6.	7.	present.	found.
10	30	0.0	0.2	1.0	1.0	1.5	1.7	1.7	0.1178	0.1179
25	30	0.0	0.3	0.5	0.5	1.0	1.5	2.0	0.1178	0.1174
40	30	1.0	1.0	0.5	0.5	0.7	1.0	1.2	0.1178	0.1178
22	5	0.0	0.2	0.3	0.3	0.2	0.2	0.8	0.1178	0.1176
25	100	0.0	1.0	2.5	2.5	2.5	0.1178	0.1180
20	30	0.0	1.5	3.5	3.5	0.0236	0.0232
20	30	0.0	0.6	2.3	3.5	0.0471	0.0470
22	30 2 cc. conc. HCl		0.0	0.6	2.5	3.0	0.0471	¹
20	30 0.004 g. Cr		0.0	1.0	3.5	3.5	0.0236	0.0230
20	30 0.02 g. Cr		0.0	0.5	1.5	2.5	3.0	3.5	...	0.0471	0.0470
23	30 1 g. Fe		0.0	0.5	1.0	2.0	3.0	3.0	...	0.0471	0.0473
23	30 2 g. Fe		0.0	0.5	1.0	2.0	2.5	0.0471	..

In Expt. 4 the end point was taken at the fourth drop. The chromium and iron were added as the corresponding alums.

As is readily seen, the deflection of the galvanometer needle caused by the addition of a given excess of ferrous sulfate (and thus the sharpness of the end point varies greatly with conditions). From the experiments given above, together with others not recorded here, we feel that this titration is favorably influenced by the following conditions:

1. Low temperature, preferably 10° C. (first three experiments).
2. High acid concentration (fourth and fifth experiments).
3. Small rather than large amounts of vanadium (second, sixth and seventh experiments).
4. Low concentration of chromic and ferric salts.

From the excellent agreement among the results, it will appear that successful determinations may be made even under the most unfavorable of these conditions if the galvanometer be closely watched. However it is obviously much easier to note large movements of the needle than small ones; and to facilitate accurate and rapid work it is desirable to fulfil the conditions for titration as outlined above.

The potentials of vanadium solutions in which the vanadium was in the quadrivalent and pentavalent states have been studied by Rutter.² He found that the potential of a platinum electrode in a solution of ammonium vanadate was 1.121 volts, taking the normal hydrogen element as zero. With a solution in which 91.9% of the vanadium was in the quadrivalent state he found the voltage to be 0.936. The e. m. f. of a solution containing no pentavalent vanadium was 0.644 volt. Beyond showing that the addition of the last portion of the reducing agent would be expected to cause a large change in the e. m. f. these measurements throw no light

¹ Not determined.

² *Z. anorg. Chem.*, 52, 370 (1907).

on the present problem. We have already pointed out that the change in potential is apparently gradual until half to three-fourths of the vanadium has been reduced, when no further change occurs until the excess of ferrous salt has been added. This corresponds to a flattening of the potential-concentration curve beginning at the point where half of the ferrous sulfate has been added, and continuing until the end point is closely approached. This, and the effect of acid concentration and temperature, Rutter's paper does not explain.

The authors hope that other experimenters in whose field this problem lies will be interested in undertaking an electrochemical study of vanadium which lately has become so important technically.

A Comparison of the Electrometric Method with Other Methods for Determining Vanadium.

Attempts to compare the electrometric end point with the ferricyanide spot plate test were given up, since it was found that at least 0.5 cc. of ferrous sulfate solution must be added above that necessary for the electrometric end point before a faint blue color was perceptible after twenty to thirty seconds. Moreover, the solution gave a faint blue color on standing one or more minutes with ferricyanide, even in the absence of ferrous iron. Thus it would appear that titrations employing this substance as outside indicator would give high results if only a short time were allowed for the indicator to act, and low values if the time allowed were longer. These comments apply, of course, only to the volumes with which we worked, 200 to 300 cc., and in which the concentration of sulfuric acid was between 10 and 25% by weight.

For the purpose of comparing the results given by other methods for determining vanadium with those given by our own method, we prepared an indeterminate solution of vanadium by dissolving a quantity of ammonium vanadate in water with the aid of a little sodium hydroxide. Analyses of this solution were then made by several of the volumetric methods most in use and by ours.

Method I. Reduction with Hydrochloric Acid.—Fifty cubic centimeters of concentrated hydrochloric acid were added to a measured volume of the solution of vanadate. This was evaporated to a small volume, the same amount of hydrochloric acid again added and the evaporation repeated. At this point 50 cc. of sulfuric acid were added and the solution evaporated until fuming was well established. (Care at this point is necessary for (1) if all hydrochloric acid is not removed it interferes with the subsequent titration of the hot solution with permanganate, and (2) if the fuming is continued too long there is danger¹ of reoxidizing the vanadium tetroxide to vanadium pentoxide by the action of the sulfur

¹ Cain, *J. Ind. Eng. Chem.*, 3, 477 (1911).

trioxide.) The solution was cooled slightly, diluted to 400 cc., warmed to 80° and titrated with potassium permanganate.

Method II. Reduction with Sulfur Dioxide.—This method was applied as recommended by Cain.¹ The vanadate solution was diluted to 350 cc., 30 cc. of H_2SO_4 (sp. gr. 1.40) added, the solution heated to boiling and sulfur dioxide, washed with water, passed in during 5 minutes. Continuing the boiling, a rapid stream of carbon dioxide, washed with sodium acid carbonate solution, was passed in during ten minutes. At the end of this time no sulfur dioxide could be detected in the steam. Water was added to make the volume 400 cc., and the temperature was then brought to 70 to 80° for the titration with potassium permanganate.

Method III. Reduction by Hydrogen Peroxide.—This method was applied substantially as recommended by Cain and Hostetter.² The solution was mixed with 30 cc. of concentrated sulfuric acid, 3 cc. perhydrol added, and the solution evaporated to the appearance of fumes. As a precautionary measure, a second portion of perhydrol was added and the evaporation repeated. (3% hydrogen dioxide may be used in place of perhydrol.) The solution was then diluted to 400 cc. volume, warmed to 80° and titrated with permanganate.

Method IV. Reduction with Oxalic Acid.—The solution was treated with 30 cc. of concentrated sulfuric acid, 0.20 g. oxalic acid added and the solution evaporated to the appearance of fumes. The fuming was continued 10 minutes, after which the solution was diluted to 300 cc., warmed to 80°, and titrated with permanganate.

Method V. Electrometric.—Titration was made at 10 to 20° with 30 cc. H_2SO_4 (sp. gr. 1.40) in a volume of 250 cc.

The ferrous sulfate and potassium dichromate solution were approximately 0.0625 *N*.

The potassium permanganate was approximately 0.1 *N* and was standardized against sodium oxalate. This solution was used to standardize both the ferrous sulfate and dichromate solutions.

Of the five different methods for determining vanadium, in our hands the electrometric method has given the most consistent results. The mean of the results obtained by our method is substantially identical with the mean of results obtained by reduction with sulfur dioxide, hydrogen dioxide and oxalic acid, but higher than that obtained by reduction with hydrochloric acid. We are at a loss to explain the discordant results obtained with hydrochloric acid as a reducing agent in the analysis of this solution, for as will be shown later it is capable of giving consistent results in other cases. Our experience with this reagent has been chiefly in the analysis of iron-vanadium alloys, in which use it has always given

¹ *Idem.*, p. 479.

² THIS JOURNAL, 34, 274 (1912).

excellent results. It may be possible that the iron or some other element present has a favorable influence upon the reduction in such instances.

TABLE II.—COMPARISON OF METHODS.

NH ₄ VO ₃ solution. cc.	Method.	Vanadium found.		Average.
		Gram.	Gram per cc.	
25	I	0.1140	0.00456	
25		0.1139	0.00456	
25		0.1164	0.00466	
25		0.1158	0.00463	0.00460
25	II	0.1170	0.00468	
25		0.1177	0.00471	
50		0.2354	0.00471	
50		0.2348	0.00470	0.00470
25	III	0.1172	0.00470	
25		0.1177	0.00471	
50		0.2360	0.00472	
50		0.2330	0.00466	0.00470
25	IV	0.1177	0.00471	
25		0.1182	0.00473	0.00472
25	V	0.1177	0.00471	
25		0.1177	0.00471	
25		0.1179	0.00472	
25		0.1174	0.00470	
25		0.1180	0.00472	
10		0.0470	0.00470	Av., 0.00471

Oxidation of Vanadium to Vanadate.

In order that the electrometric titration of vanadium may be applied to the analysis of ores and metals, it is necessary to have some convenient quantitative method for insuring oxidation of the vanadium to vanadate. It is further necessary that the solution as prepared shall contain no substance other than the vanadate which may be reduced by ferrous sulfate.

Nitric acid was tried as an oxidizing agent and at first seemed to be quite promising, especially as chromium seems not to be oxidized under the most vigorous oxidizing conditions, while vanadium is quite rapidly oxidized. We were eventually disappointed, however, for the oxidation was invariably incomplete, as is shown in the following experiment:

A vanadium solution was prepared by dissolving ferro-vanadium in a mixture of dilute sulfuric and nitric acid. This was evaporated until fumes appeared and diluted with water. This solution, when reduced with either hydrochloric acid or hydrogen dioxide, was found to be of such strength that 10 cc. required 17.7 cc. of our permanganate solution for its oxidation. In our experiments, 10 cc. portions of the solution were reduced with a slight excess of ferrous sulfate solution and 45 cc. of sulfuric acid (sp. gr. 1.4) and 50 cc. of water added. Different amounts of nitric acid were then added and the solutions boiled for varying lengths of time. The solutions were then cooled slightly and titrated with per-

manganate, the amount of permanganate required being a measure of the failure of the nitric acid to oxidize the vanadium.

TABLE III.—OXIDATION OF VANADIUM BY NITRIC ACID.

HNO ₃ cc.	Period of boiling. Min.	KMnO ₄ used. cc.	% oxidation.
0	0	17.7	..
5	5	6.0	66
10	5	2.0	89
15	5	1.5	91.5
5	15	5.0	72
10	15	1.8	90
15	15	1.0	94
10	20	0.4	97.7

From the above it will be clear that nitric acid could not be depended upon to oxidize the vanadium. Nitric acid also was found to produce a harmful effect upon the electrometric titration, probably by reaction with FeSO₄. This was less noticeable with low acid concentration and low temperatures. The trouble manifested itself in the irregular behavior of the galvanometer, in that the addition of ferrous sulfate would cause a movement of the needle indicating that the end point had been reached, but, after a moment, the needle would return to its original position. This would occur repeatedly, requiring the addition of a large excess of ferrous sulfate. The influence of the acid concentration is shown in Table IV.

TABLE IV.—EFFECT OF NITRIC ACID ON TITRATION.

Temperature 20°. Total volume 100 cc.

HNO ₃ ¹ cc.	H ₂ SO ₄ (Sp. gr. 1.40). cc.	Electrometric titration		Corrected Vol. FeSO ₄ . cc.	Vanadium		Remarks.
		FeSO ₄ . cc.	K ₂ Cr ₂ O ₇ . cc.		present. G.	found. G.	
2.5	10	35.30	0.20	35.10	0.1026	0.1025	good
10	10	35.30	0.25	35.05	0.1026	0.1022	end point
10	45	No end point could be found					
10	45						

We thought to complete the oxidation with nitric acid by evaporating to the appearance of fumes, which would also avoid the difficulty of titrating in the presence of much nitric acid. To test this, we oxidized 10 cc. of our vanadium solution with permanganate to a faint pink, added 40 cc. of sulfuric acid (sp. gr. 1.40) and evaporated to the fuming point. When cooled and titrated electrometrically the vanadium found was 0.0955 g. instead of 0.1026 g., showing that the vanadate had been reduced by the treatment. Another similar portion treated with 40 cc. of sulfuric acid and 60 cc. of water was made barely pink with permanganate. After boiling 15 minutes, the solution turned pink on the addition of the first drop of permanganate, showing that simply boiling with dilute sulfuric acid had no reducing effect on the vanadium. It is possible that

¹ The nitric acid used here is in excess of that necessary for oxidation.

dust in the sulfuric acid caused the liberation of sulfur dioxide which in turn caused the reduction of the vanadate. For these reasons all attempts to oxidize vanadium with nitric acid were abandoned.

Oxidation with Permanganate.

Vanadium may be completely oxidized to the pentavalent condition in hot solution by potassium permanganate, as is well known. The method chosen to accomplish this in the absence of chromium was to treat the solution at 80° with dilute potassium permanganate solution until a slight permanent pink color resulted. The solution was then treated with a few drops of hydrochloric acid (1 to 3), and boiled for five minutes. All of the potassium permanganate was thus decomposed and the chlorine removed, the vanadate remaining unchanged. As an alternative to this method, the permanganate may be added carefully to the hot solution until the first change of color appears. This point may be found very accurately and in fact most of the volumetric methods for determining vanadium depend upon it. The solution, after cooling to 20° or lower, is ready to titrate electrometrically. The last process is available for use when small amounts of chromium are present.

Oxidation with Ammonium Persulfate.

This method involves oxidation with ammonium persulfate in the presence of silver nitrate. To carry out the process, the solution containing the vanadium is treated with nitric acid to oxidize the iron. Enough sulfuric acid is added to make the total present equal to 25 to 40 cc. of acid of sp. gr. 1.40. The solution is then diluted to a volume of 300 cc. with hot water and 10 cc. of solution of silver nitrate (2.6 g. to 1 liter) and 5 g. of ammonium persulfate added. After boiling the solution for ten minutes it is treated with 5 cc. of dilute hydrochloric acid (one to three). Five minutes' boiling decomposes the permanganic acid which will form if manganese is present. The solution was then cooled and titrated electrometrically.

The Determination of Vanadium in the Presence of Chromium.

Of the methods given below for the oxidation and determination of vanadium only one is available in the presence of chromium. This follows from the fact that reagents which oxidize vanadium completely tend to oxidize chromium, at least in part. We were, therefore, unable to accomplish the oxidation by ammonium persulfate or permanganate in excess even though the solution were subsequently boiled with hydrochloric acid. The method which we were able to use involves oxidation of the hot solution with permanganate to the first change of color, taking care not to add an excess. An account of our experimental work in the application of this method will be given in a paper which we expect shortly to publish on the analysis of chrome-vanadium steels.

TABLE V.—ANALYSIS OF SOLUTIONS OF FERRO-VANADIUM¹ (METHODS I-IV).

Solution A.				Solution B.				
Vanadium.				Vanadium.				
Cc. soln.	Found. G.	Wt. per cc. G.	Av. per cc.	Cc. soln.	Found. G.	Wt. per cc. G.	Av. per cc.	
25	0.2575	0.01029	0.01027	200 I	0.3861	0.00193(0)	0.00193(2)	
25	0.2572	0.01029		200 I	0.3866	0.00193(3)		
10	0.1030	0.01030		50 III	0.0970	0.00194(0)		
10	0.1020	0.01020		50 V ⁴	0.0966	0.00193(1)		
10	0.1029	0.01029	0.01032	50 V ³	0.0963	0.00192(6)	0.00182(5)	
10	0.1023	0.01023		Solution C.				
25	0.2590	0.01036		200 I	0.3652	0.00182(6)		
25	0.2596	0.01038		200 I	0.3640	0.00182(0)		
10	0.1038	0.01038	0.01027	50 III	0.0907	0.00181(5)		
10	0.1030	0.01030		50 V ⁴	0.0915	0.00183(0)		
10	0.1022	0.01022		50 V ³	0.0917	0.00183(5)		
10	0.1025	0.01025	0.01025					
10	0.1025	0.01025						

Summary.

(1) Vanadates may be successfully titrated with ferrous sulfate, using a change in the electromotive force of a suitable cell as the indicator.

(2) The most suitable conditions for obtaining a quick and accurate determination by this method have been defined.

(3) Several interesting theoretical problems which arise from a study of the change of potential during the titration are indicated.

(4) A comparison has been made of four of the methods in widest use for the determination of vanadium and the results are found to be in close agreement with those found by the method here outlined.

(5) The oxidation of vanadium to the pentavalent condition with nitric acid has been found unsatisfactory for quantitative purposes.

(6) The oxidation with potassium permanganate or ammonium persulfate has been found entirely satisfactory for this method in the absence of chromium.

(7) The method has been applied to the analysis of ferro-vanadium and with small changes in the preparation of solutions could be applied to the analysis of ores.

RESEARCH DEPARTMENT OF THE MIDVALE STEEL COMPANY,
PHILADELPHIA, PA.

¹ These solutions were prepared by dissolving ferro-vanadium in dilute sulfuric acid, using about 10 cc. of sulfuric acid of sp. gr. 1.40 in 100 cc. or less of water for each gram of the alloy. When solution was complete, nitric acid was added in small amounts to oxidize the iron and break up carbides of vanadium. 200 cc. of Solutions B and C correspond to 1 gram of ferro-vanadium.

² Oxidized with KMnO_4 to a faint pink color.

³ Oxidized with KMnO_4 and boiled with a little dilute HCl .

⁴ This solution was oxidized with ammonium persulfate in the presence of silver nitrate as described on p. 350.

THE COLORIMETRIC DETERMINATION OF ACETYLENE.

By E. R. WEAVER.¹

Received October 14, 1915.

CONTENTS.—1. Introduction. 2. Development of Method. 3. Procedure for the Determination of Acetylene: (a) Preparation of Absorbing solution; (b) Absorption of Acetylene; (c) Dilution and Comparison with Color Standard. 4. Preparation and Standardization of a Color Standard. 5. Applications of Proposed Method: (a) Determination of Acetylene in Gas Mixtures; (b) Determination of Water. 6. Summary.

1. Introduction.

In the course of experiments on the qualitative detection of small amounts of water² it was found that the addition of alcohol or acetone containing dissolved acetylene to a solution of cuprous chloride, or the absorption of acetylene in a cuprous chloride solution containing alcohol or acetone, resulted in the formation of a clear colloidal solution of an intense red color. The formation of a red colloid when a small amount of cuprous chloride is added to a solution of acetylene in water was observed by Küspert,³ but no attempt to use the reaction for analytical purposes appears to have been made by him or others. Since the reaction appeared to present possibilities as a direct colorimetric method for the determination of water, an effort was made to apply it for this purpose. The results first obtained were very discordant and it soon became apparent that a careful examination of all the factors which could affect the results would be necessary before any satisfactory procedure could be devised. The investigation of these factors has resulted in the development of a quick and very sensitive method for the determination of acetylene. The application of this method to the determination of water, especially the determination of very small amounts in materials of high purity which was the primary object of the investigation, has been much less successful; some of the difficulties encountered will be described in the latter part of the paper (p. 359).

The formation and properties of a colloidal solution are influenced by so many factors that more than five hundred experiments were required to determine the effect of each factor and to devise a method which will give uniform results.

Lack of space prevents the publication, here, of more than an outline of the experimental work; but a more complete account will soon be published as a Scientific Paper of the Bureau of Standards.

2. Development of Method.

The method was developed by the preparation of colloidal solutions from known amounts of acetylene, secured by measuring from any ordinary buret into a distilling flask a standard solution of acetylene in ether.

¹ Published by permission of the Director of the Bureau of Standards.

² THIS JOURNAL, 36, 2462-8 (1914).

³ Z. anorg. Chem., 34, 453-4 (1903).

The use of such a solution seemed especially desirable since it eliminated the variables affecting the amount of acetylene evolved from a constant weight of water when reacting with calcium carbide, and at the same time permitted an exact duplication of the conditions which appeared to be most favorable for the quantitative evolution and determination of acetylene from small amounts of water, *i. e.*, solution in ether with subsequent distillation, in a stream of hydrogen, into the absorbing solution. This made the results applicable in the investigation of the water method itself.

The standard solution of acetylene in ether was prepared by passing into 500 cc. of ether, for several minutes, a stream of acetylene which was generated from specially prepared calcium carbide and washed with water. The solution was then diluted with ether sufficiently for use. The carbide used was prepared for this purpose by Dr. C. W. Kanolt, of this Bureau from pure precipitated calcium carbonate and a considerable excess of sugar charcoal. The solution of acetylene in ether was standardized gravimetrically by precipitation with ammoniacal cuprous chloride and subsequent determination of copper in the precipitate. In making this determination, it was found absolutely necessary to exclude air from the apparatus in which the precipitate is produced and washed. Otherwise part of the copper goes into solution. This precaution is ignored in most, if not all, of the published methods for making this determination.

The influence of the variable factors affecting the formation of the colloidal solution was investigated by absorbing definite amounts of acetylene, from measured volumes of the standard solution, in 30 cc. of absorbing solution. After the absorption was completed this solution was diluted to 100 cc. before comparing with a color standard in a colorimeter of simple construction. From a consideration of the results of these experiments the following method was chosen. The necessary directions are given in italics. Comments are given in the ordinary type.

3. Procedure for the Determination of Acetylene.

(a) **Preparation of Absorbing Solution.**—*Dissolve 0.25 g. of gelatin in hot water, dilute to 500 cc., and add 500 cc. of 95% alcohol and 1.25 g. of hydroxylamine hydrochloride. To 20 cc. of this solution add 10 cc. of concentrated ammonium hydroxide and a small amount of cuprous chloride. One- or two-hundredths of a gram of cuprous chloride is all that is required although as much as half a gram is not objectionable. If a greater amount of solution is required to fill the absorption apparatus it should be made up in the same proportions.*

Several substances have been tried as protective colloids besides gelatin, but all have been found unsuitable. More than the above amount of gelatin is not required and much more is objectionable, since it may

be precipitated by the alcohol and the various salts in solution. A large amount of alcohol in the solution favors completeness of absorption and uniformity of results, but too large an amount precipitates the gelatin from solution. The amount of ammonia in solution must be regulated rather carefully. Either too little or too much ammonia results in the formation of a precipitate and in incomplete absorption. The presence of ammonium chloride or other strong electrolyte causes coagulation and erroneous results; an excess of hydroxylamine salts should be avoided for the same reason, but more than the amount given in the above directions may be used if required to completely discharge the blue color of cupric-ammonium salts. It is best, however, to add any excess of hydroxylamine necessary to decolorize, when diluting with water after absorption, rather than before; the presence of a small amount of cupric salts during the absorption does not affect the results.

(b) **Absorption of Acetylene.**—*The gas to be tested for acetylene should be bubbled at a moderate rate into a rather small volume of the absorbing solution through a glass tip with a small opening.* The effect of changing the volume of the absorbing solution is shown in Table I. In each case the composition of the absorbing solution was the same and the solution was diluted to 100 cc. before making the colorimetric comparison. Since these experiments were very carefully made after the effect of all other variables had been investigated, the tendency to obtain higher results when using the smaller volume of absorbing solution is probably not due to experimental error. It is believed that this effect is due to equilibrium within the solution, the significance of which will appear later.

TABLE I.—EFFECT OF VOLUME OF ABSORBING SOLUTION.

Volume of absorbing solution. cc.	Acetylene.		Difference.
	Present. Mg.	Found. Mg.	
30	0.68	0.71	+0.03
30	0.41	0.41	±0.0
30	0.54	0.55	+0.01
30	0.27	0.26	—0.01
60	0.41	0.38	—0.03
60	0.54	0.53	—0.01
60	0.27	0.24	—0.03
90	0.41	0.38	—0.03

It is important that a small tip be used for introducing the gas into the solution. In the experimental work two tips were used for this purpose, one having an internal diameter of about 2 mm. and the other a diameter of about 0.2 mm. It was found that 30 to 50% of the acetylene escaped when using the larger tip at rates of from 30 cc. to 75 cc. per minute. There was no indication of loss of acetylene when using the small tips at rates up to 50 cc. per minute, and loss of acetylene did not exceed 10% even when the rate was 100 cc. per minute.

(c) **Dilution and Comparison with Color Standard.**—*After the absorption of the acetylene, the colloidal solution is diluted with water to a convenient volume and compared in a colorimeter with a color standard of fixed value, which may be a fixed depth of a solution of a red dye or a piece of ruby glass. The value of the standard must be determined by previous calibration with known amounts of acetylene.* A large number of experiments have shown that, within the limit of accuracy of the colorimeter readings, it is immaterial how much the colloidal solution is diluted before the readings are taken, provided the volume of solution is taken into account in calculating the amount of acetylene. For example, if a sample of acetylene is absorbed in 30 cc. of solution and the resulting liquid successively diluted with water to 60, 90, 120 cc. and comparisons with the same color standard are made at each dilution, it will be found that the depths of colloidal solution required to match the standard are in the ratios 1 : 2 : 3 : 4.

4. Preparation and Standardization of a Color Standard.

The most satisfactory standard for use in colorimetric work is of course a solution having a known value and of the same character as the solution whose value is to be determined. Unfortunately, however, a colloidal solution of copper carbide cannot be preserved for any considerable length of time and it is quite difficult to prepare one of known value. The color of colloidal solutions prepared under different conditions varies widely, and those produced by the action of an excess of acetylene on small amounts of a copper salt cannot be compared accurately with the colloids prepared from small amounts of acetylene and an excess of the copper salt.

It is possible, however, to match the colloidal solution with a solution of red dye or a piece of ruby glass. The standard solution used for comparison in the experimental work had the following composition:

Chromanilbraun R.....	0.21 mg.
Carmoisine B.....	0.04 mg.
Gum arabic.....	2.5 g.
Water.....	100 cc.

This solution was designated on an arbitrary color scale as standard "H 25" and will, for the sake of brevity, be so designated in this discussion.

Although it is possible to match very closely any depth of a given colloidal copper carbide solution with a dye solution, such as solution "H 25," the ratio between the depths of the two solutions is not constant but varies with the depth. When comparing small depths, the color, *i. e.*, the relative amount of light of the longer and shorter wave lengths transmitted, is the determining factor in making the comparison. When a greater depth is used, practically all light except red is excluded and the

point of agreement is no longer determined by the color of the two fields in the colorimeter, but by whether one field is lighter or darker than the other.

Upon plotting the results of any series of comparisons of the colloidal solutions produced by known amounts of acetylene with a fixed color standard it appears that, within the limits of experimental error, the results obtained with all lie on a straight line represented by the equation

$$x = ay + b,$$

in which x = amount of acetylene, $y = \frac{1}{\text{depth of colloidal solution}}$, and

a and b are constants. In this equation b represents, of course, the point at which the curve cuts the horizontal axis and its value is that of the smallest amount of acetylene which will produce a color in the absorbing solution. The value of a is dependent upon the color standard used. Both constants must be experimentally determined.

When a variable depth of a standard solution is used for the comparison, the ratio $\frac{\text{depth of standard solution}}{\text{depth of colloidal solution}}$ may be used as the value for y

and the equation $x = ay + b$ still holds, provided the ratio between the depths of the two solutions is the same for all depths. As pointed out in the preceding section, this is not the case with any of the solutions used as standards, but it may be assumed without appreciable error for amounts of acetylene not greater than 0.1-0.2 mg. For larger amounts a constant depth of standard solution should be used in order to provide a color standard of fixed value.

The value of b was at first thought to represent the minimum concentration of acetylene in the gas mixture which would be absorbed by the solution. If the existence of such a minimum were the true explanation of the fact that the curve does not pass through the origin, it is evident that a given amount of acetylene diluted with a large volume of hydrogen would give lower results than the same amount of acetylene diluted with a small volume of hydrogen. That such is not the case was clearly shown by experiments. The only other probable explanation seemed to be that there is an equilibrium in the absorbing solution and that b represents the minimum concentration of dissolved acetylene which will produce a colored colloid. If this is true the value of b should be proportional to the volume of absorbing solution. The experiments given in Table I and plotted in Fig. 1 show that this relation is at least approximately correct.

Fig. 2 shows the results of one series of comparisons of "standard solution H 25" with known amounts of acetylene from a carefully analyzed solution in ether. The equation of the straight line averaging these

values is $x = 1.43 y + 0.03$, where x is expressed in tenths of a milligram of acetylene and y is the ratio $\frac{\text{depth of standard solution}}{\text{depth of colloidal solution}}$.

Calibration of any Color Standard.—Since the value of b depends upon the volume of the absorbing solution and is independent of the color standard used, its value may be experimentally fixed once for all. This value has been carefully determined several times under different conditions and has always been found to be between 0.02 and 0.05 mg. It seems probable that, in any operations in which there is fairly complete absorption, the value of b may be assumed to be 0.03 mg. for 30 cc. of absorbing solution without causing any error in excess of 0.01 mg. In order to calibrate any color standard it is then only necessary to make one accurate comparison of the standard with a colloidal solution prepared from a known amount of acetylene. This comparison gives simultaneous values for x and y in the equation $x = ay + 0.03$, and the value of a may be

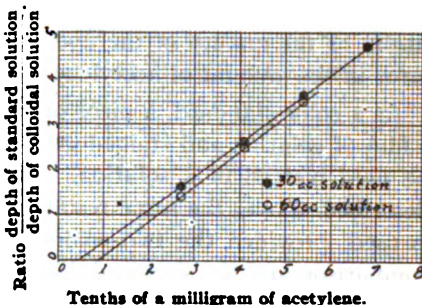


Fig. 1.—Effect of volume of absorbing solution.

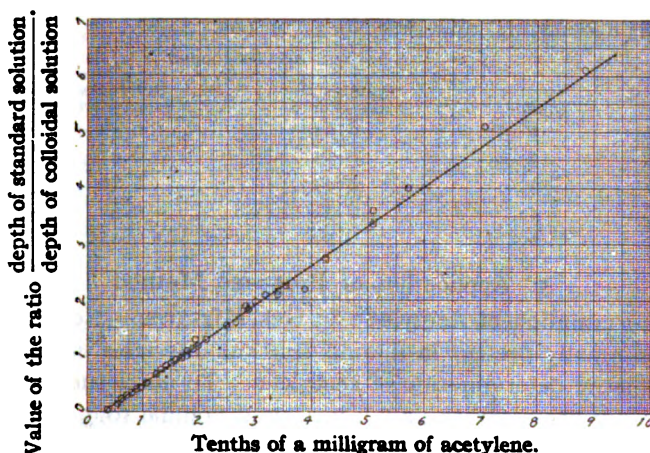


Fig. 2.—Result of one series of comparisons using "standard H 25" and known amounts of acetylene. Equation of straight line is $x = 1.43 y + 0.3$.

easily calculated. Unknown amounts of acetylene may then be determined for the same equation, using the values already found for a and b , or, for convenience, a curve may be plotted and values taken from that.

Chemists who desire to make only an approximate determination without the labor of previously calibrating a standard, may do so by

using as a standard a depth of 10 cm. of a solution of 0.04 g. of azolitmin in 100 cc. of water. The value of a for a solution of this strength made from a sample of the dye of Kahlbaum grade was found to be 0.13 mg. It is not known how much variation will be found among different samples of azolitmin; but it is apparent from the slope of a curve for azolitmin given in the complete paper, that any variation in the strength of the azolitmin or the quality of the dye will cause much less than a proportional error in the amount of acetylene found.

As a color standard, a piece of ruby glass or a glass plate covered with a film of gelatine and stained with oxamine red or other suitable dye may be used instead of a solution. Once having calibrated the standard as described above, the same results are obtained no matter what standard is used, provided the two colors are enough alike to permit an accurate comparison and the standard does not change. A ruby glass is, of course, permanent, but the author is unable to say how much reliance may be placed in the permanence of color of a stained film.

Table II gives the results of a series of determinations of unknown amounts of acetylene using two different standards for comparison. The results are in substantial agreement.

TABLE II.

Determination of unknown amounts of acetylene, using as standards: (1) 10 cm. solution H 25 $a = 1.43$; (2) ruby glass No. 1 $a = 3.69$.

Sample.	Acetylene found.	
	Solution H ₂₅ as standard.	Ruby glass as standard.
1	0.51	0.55
2	0.43	0.41
3	0.29	0.28
4	0.57	0.56
5	0.56	0.55

5. Application of Proposed Method.

(a) **Determination of Acetylene in Gas Mixtures.**—None of the constituents normally present in illuminating gas interferes in any way with the colorimetric determination of acetylene. To make such a determination it is only necessary to pass a measured volume (0.5–2 liters) of the gas into the absorbing solution and make the colorimetric comparison. The whole determination can be made in about ten minutes. Four successive determinations of the acetylene in illuminating gas taken directly from the house piping gave 0.30, 0.30, 0.32 and 0.33 cc. per liter. The method was applied by Mr. J. D. Edwards in this laboratory to the testing of hydrogen of high purity. One part of the acetylene was readily determined in 250,000 parts of the hydrogen from one source. Hydrogen from another source, believed to contain only a small fraction of this

amount of acetylene, produced a red stain on the tip of the inlet tube in the absorbing solution, but no coloration in the liquid.

In order to ascertain whether acetylene could be determined in air by this method, a sample of the acetylene solution in ether was first run in the usual manner with a stream of hydrogen to carry it into the absorber; then the determination was repeated with the same amount of acetylene and a stream of air instead of hydrogen. The acetylene-air mixture was passed through a strongly alkaline solution of pyrogallol and thence into the absorber; and the pyrogallol solution was heated to boiling before the stream of air was stopped. When hydrogen was used the test showed 0.56 mg. of acetylene; with air 0.53 mg. of acetylene was found.

The experiment also proved that a solution of potassium hydroxide could be used if necessary to remove hydrogen sulfide, carbon dioxide, or similar interfering gases. It was found by several experiments that small amounts of carbon dioxide did not affect the determination, but that larger amounts had the same effect as the introduction of a small amount of a strong electrolyte into the solution. The color of the colloid produced by acetylene carried over in a stream of pure carbon dioxide was too brown to admit of any accurate comparison.

(b) **Determination of Water.**—The determination of small amounts of water by the colorimetric method, which was the primary object of this investigation, presents several difficulties which are nearly insurmountable.

Efforts were made to determine water in a variety of materials by the use of the apparatus described below. The sample to be tested was brought into contact with calcium carbide, in a small glass apparatus, either with or without anhydrous ether to act as a solvent. The flask in which the reaction took place was connected to a condenser and thence to a tube filled with carbide to prevent the escape of water vapor. Ether dried over sodium could be introduced directly or could be distilled through a phosphorus pentoxide tube into the reaction flask. The whole apparatus could be swept out with hydrogen dried over phosphorus pentoxide.

The greatest difficulty encountered is due to the fact that calcium carbide itself, or the calcium hydroxide which it always contains, appears to occlude acetylene, which it holds with great tenacity but gives off slowly for long periods. It may be that the source of trouble is a small amount of water which is held by the calcium hydroxide and which reacts with the carbide very slowly. Whatever the exact cause, there is no question that with any carbide obtainable commercially all efforts to remove this acetylene by ignition or evacuation have proven unsuccessful. The acetylene which causes the trouble may be removed by boiling the car-

bide two or three times with an anhydrous liquid such as ether. After such treatment the carbide must not be exposed to the air even for an instant. After the reaction between the carbide and the sample being tested for water is finished, it is necessary to remove the acetylene produced in the same way as before the test. It is apparent that a considerable amount of ether is required for the two purposes and that a large volume of hydrogen is required to sweep out the apparatus completely. It has been found almost impossible to dry ether so thoroughly that the amount required by this test will produce no acetylene which can be detected. Even the ether from a bottle entirely filled with a loose mass of sodium wire which remains apparently perfectly bright may produce a surprising amount of acetylene, and phosphorus pentoxide appears to lose very quickly its power to remove the water completely from ether vapor. It is consequently very difficult to secure consistent blanks.

A second source of difficulty, which has been recognized by every chemist who has used the carbide method for the determination of water, is the fact that the theoretical amount of acetylene is never produced from a known quantity of water. This is particularly true when dealing with very small amounts of water. In the author's experiments the amount of acetylene produced has varied from 50-80% of the theoretical, generally approaching the latter figure.

In consequence of these sources of difficulty and error, tests made with the colorimeter have little more significance than the much simpler qualitative tests described in an earlier paper.¹ A negative test is quite conclusive, but the detection of an amount of acetylene less than 0.1 mg. has little more than qualitative significance.

Negative tests have shown that the standard samples of benzoic acid, naphthalene and sugar issued by this Bureau are almost absolutely anhydrous. As an example of the kind of results which may be expected when water is present, the following tests are given of a sample of alcohol in which Mr. E. C. McKelvy, of this Bureau, had determined the amount of water by the method of critical solution temperature.²

TABLE III.—DETERMINATION OF WATER IN ALCOHOL.

Found by critical solution temperatures.		Found by colorimetric method.		
Water = A.		Acetylene.	Water = B.	
Mg.		Mg.	Mg.	B X 100/A.
1.0		0.48	0.62	62
1.0		0.58	0.80	80
6.0		3.5	4.8	80
6.0		3.6	5.0	82
50		21.2 ³	29.2	59

¹ THIS JOURNAL, 36, 2462-8 (1914).

² Bull. Bur. Standards, 9, p. 344.

³ Acetylene determined gravimetrically.

6. Summary.

A colorimetric method for the detection of small amounts of acetylene has been developed in the course of an investigation upon the determination of small amounts of water by the use of calcium carbide. The results upon the determination of water have not been satisfactory, but the method for acetylene has been worked out successfully.

The determination is carried out by conducting the gas to be investigated into an ammoniacal solution of cuprous chloride containing gelatin and alcohol, and comparing the red colloidal solution so obtained with a suitable standard, which may be either a solution of red dye or a piece of ruby glass.

After a careful investigation of the effect of varying the composition of the absorbing solution, the following procedure was adopted in making up the solution: Dissolve 0.25 g. of gelatin in hot water, dilute to 500 cc., and add 500 cc. of 95% alcohol and 1.25 g. of hydroxylamine hydrochloride. To 20 cc. of this solution add 10 cc. of concentrated ammonium hydroxide and a small amount of cuprous chloride. After the absorption of the acetylene, the solution is diluted to 100 cc. and compared in a colorimeter with the standard which has been chosen. The standard used in the experimental work was a solution containing chromanilbraun R, carmoisine B and gum arabic. A more convenient, though less accurate, standard is a fixed depth of a solution of azolitmin. If 10 cm. of a solution of azolitmin containing 1 part of the dye to 2500 parts of water is used as standard, the amount of acetylene in 100 cc. of colloidal solution may be calculated from the equation $x = 0.13 y + 0.03$, where x = no. of milligrams of acetylene and y = 1 ÷ no. of centimeters of colloidal solution required to match the standard.

The method is very sensitive. Amounts of acetylene as small as 0.03 mg. may be detected and amounts up to 2 mg. determined with an accuracy of better than 0.05 mg. Several applications of the method are described.

Hydrogen sulfide, and large amounts of oxygen and carbon dioxide interfere with the test, but all of these may be removed by passing the gas to be tested through a hot alkaline solution of pyrogallol without loss of acetylene.

The investigation required some experiments upon the determination of larger amounts of acetylene by precipitation with cuprous chloride and subsequent determinations of the copper. It was found that in order to obtain accurate results by this method it is absolutely necessary to carry out the filtration and washing of the precipitate in the absence of air.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

ANODIC RELATIONS OF PASSIVE IRON WITH NOTES ON POLARIZATION POTENTIALS AS INFLUENCED BY EXTERNAL GAS PRESSURES.

BY H. G. BYERS AND SETH C. LANGDON.

Received October 11, 1915.

In a series of researches previously carried out in this laboratory,¹ it was determined that the establishment of anodic passivity in iron is influenced by the seven following factors: (1) the condition and previous treatment of the iron, (2) the nature and concentration of the electrolyte, (3) the stirring of the electrolyte, (4) the temperature, (5) the current density, (6) the time of flow of the current, and (7) the concentration of oxygen dissolved in the electrolyte.

The last factor was of striking interest, for it was found that with a pure iron anode, of 0.71 mm. diameter and 5 mm. in length, immersed in 0.2 *N* H₂SO₄ at a temperature of 0° C., with negligible stirring influences, and with 15 milliamperes flowing, it required 45 seconds for passivity to be established, that is, if the electrolyte was saturated with oxygen at 3 pounds pressure per square inch, but only 4 seconds were required if the electrolyte was saturated with oxygen supplied at a pressure of 81 pounds per square inch.

That the effect was due to the high concentration of dissolved oxygen, and not to the mechanical pressure, was shown by the failure of other gases, supplied at high pressure, to produce any corresponding effect.

Since it has been assumed that the anodic potential is a measure of passivification, it was expected that illuminating results would be obtained by a study of the effect of oxygen pressure on the potential of iron.

In order that the results obtained might be of greater value in interpreting the work already done, conditions analogous to those outlined above were chosen, *i. e.*, the same electrolyte, temperature, concentration, similar electrodes, etc.

In order to work with the high gas pressure the normal calomel electrode was modified somewhat in form, as shown in Fig. 1. The absence of air space within the cell prevents liquids from being forced back into the cell when pressure is applied. The fine capillary minimizes diffusion, and as fresh normal potassium chloride was introduced through the stopcock, after each set of measurements, any contaminated solution in the capillary was thus forced out. During the six months that the cell was in use its value was checked from time to time and showed very satisfactory constancy. Throughout the work a potentiometer, capable of detecting potential differences of one ten-thousandth of a volt, was

¹ Byers, *THIS JOURNAL*, 30, 1718 (1908); Byers and Langdon, *Ibid.*, 35, 759 (1913); 36, 2004 (1914).

used, but readings were taken only to the third decimal, for in most cases the potential fluctuates slightly from moment to moment. The instrument used was very satisfactory as it allowed very quick and accurate adjustment.

The initial electromotive force of different sections of wire, immediately after immersion in 0.2 *N* sulfuric acid was not always the same, but ranged between the limits +0.522 and +0.506 volt. This behavior, which is probably to be ascribed to variations in the material and surface of the electrodes, finds analogy in the variation of the time required for a given current to passivify different sections of wire.

As iron stands in contact with the acid its potential gradually changes, as shown in Table I, though the variations here are of a more uniform character and of greater magnitude than were shown in all cases.

TABLE I.

Time in minutes.....	Start	2	19	31	37	45
E. M. F. Volts.....	+0.511	+0.513	+0.523	+0.524	+0.524	+0.527
60	72	87	125	140	150	152
+0.530	+0.536	+0.536	+0.539	+0.542	+0.544 ¹	+0.549
					+0.549	+0.550

An exactly similar set of figures appears in Table II where at the end of seven minutes hydrogen gas, at 50 lbs. pressure per sq. inch, was applied. As a comparison of Tables I and II shows, the gas at this pressure caused no noticeable deviation from the normal behavior. Oxygen pressure showed a corresponding lack of effect (see Table II) on prolonged application, thus allowing the electrolyte to become saturated with the gas.

TABLE II.

Time in minutes.	E. M. F.		Time in minutes.	E. M. F.	
Start	0.507	No	Start	0.510	No
2	0.510	ext.	4	0.514	ext.
4	0.511	gas	7	0.515	pressure
7	0.513	pressure	8	0.517	
10	0.515		9	0.519	
12	0.517	Hydrogen	13	0.521	Oxygen
13	0.518	pressure	18	0.523	pressure
15	0.518	50 lbs.	19	0.524	53 lbs.
18	0.519	per sq.	20	0.524	per sq.
20	0.520	in.	25	0.526	in.
			27	0.527	

It may therefore be concluded that neither mechanical pressures nor the saturation of the electrolyte with hydrogen or oxygen produces a pronounced effect on the electromotive force of iron when immersed in 0.2 *N* sulfuric acid.

The second step was to obtain the electrode potential of iron electrodes held in the passive condition by a small current, and subsequently to de-

¹ Iron changed to fresh electrolyte.

termine the effect of oxygen and other gaseous pressures. The apparatus is shown in Fig. 1, and requires but little explanation. The iron electrode was in series with a platinum electrode, a milliammeter, five lead storage

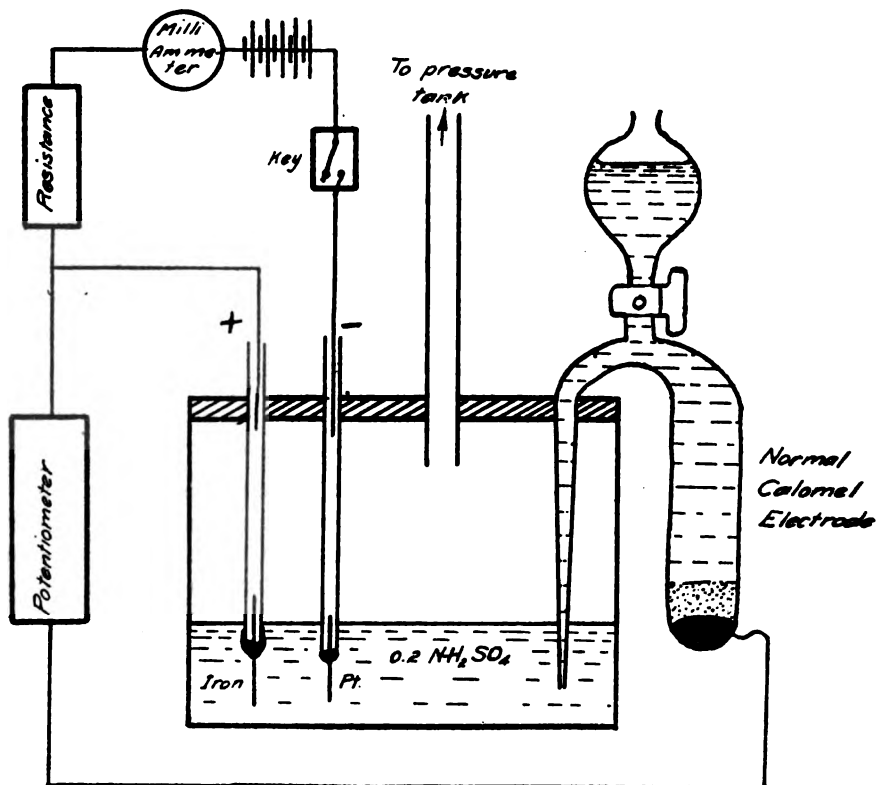


Fig. 1.

batteries, a variable resistance and a key. The potential difference between the normal calomel electrode and the iron electrode could be measured at any time by the potentiometer which was connected through a commutator.

With the arrangement just described, a section of wire was rendered passive at high current density and then the resistance of the external circuit increased until the polarizing current had dropped to 10 milliamperes. The first readings of the potential just after passivification were always higher than subsequent values. These changes, as appears in Table III, show that a polarized passive electrode becomes less noble on standing, even though a small external current is maintained to sustain the polarization. This is exactly analogous to the behavior of the active iron when no external current is used. (Compare Table I.)

TABLE III.

Iron passive. 10 M. A. flowing.

Time	Start	4	7	10	16	20	22	24 min.
E. M. F.	+0.510	+0.512	-1.790	-1.789	-1.785	-1.782	-1.783	-1.781

The effect on this polarization potential produced by the application to the surface of the electrolyte, of oxygen gas under pressure, is shown in Table IV, where it is clearly evident that, coincident with the rise in pressure, there is a fall in potential, and that with the release of the pressure the potential again rises, but not as high as it was when the pressure was first applied.

TABLE IV.

Time in minutes.	E. M. F.	Ext. current.	O pressure applied. Lbs. per sq. in.	Time in minutes.	E. M. F.	Ex. current.	O pressure applied. Lbs. per sq. in.
Start	+0.506	None	None	30	-1.788	10 M. A.	42
1	+0.560	"	"	32	-1.786	"	"
2	+0.507	"	"	33	-1.788	"	"
Iron rendered passive and then current reduced to 10 M. A.				36	-1.796	"	None
3-5	Varying	10 M. A.	"	38	-1.798	"	"
7	-1.820	"	"	39	-1.796	"	"
10	-1.816	"	"	41	-1.796	"	"
12	-1.818	"	"	43	"	48
15	"	42	44	-1.786	"	"
17	-1.806	"	"	46	-1.787	"	"
22	-1.807	"	"	48	-1.788	"	"
23	"	None	53	-1.793	"	"
25	-1.811	"	"	54	+0.518	None	None

This is not surprising in view of the fact just established in the previous experiment, that for an anodically polarized passive iron electrode the value of its potential gradually decreased with time.

That the change in potential is due to the mechanical pressure and is independent of the nature of the gas is also made clear by the data in Table V. A range of oxygen pressures was used and then a corresponding treatment using hydrogen pressure. The results as shown here are more uniform than those exhibited by most electrodes. The measurements in the table were all made on one section of iron wire but the data indicated were previously ascertained on divers sections and the results as shown are typical and are confirmed by numerous independent tests. The table shows the most complete and satisfactory single series of measurements.

When this work was undertaken it was expected that if the gas pressure produced any effect it would be after the electrolyte had become saturated with the gas, and that if the hydrogen produced any result at all that it would be opposite to that caused by oxygen. The fact that the change

TABLE V.

Time in minutes.	E. M. F.	Ext. current.	O press. applied. Lbs. per sq. in.	Time in minutes.	E. M. F.	Ext. current.	O press. applied. Lbs. per sq. in.
Start	+0.510	None	None	27	-1.770	10 M. A.	None
3	+0.510	"	"	28	-1.760	"	25.8
5	+0.510	"	"	30	-1.751	"	30.5
Iron rendered passive current then lowered to 10 M. A.				31	-1.740	"	34.6
8	-1.784	10 M. A.	"	32	-1.730	"	43.9
12	-1.771	"	"	34	-1.767	"	None
13	-1.771	"	"	35	+0.520	None	"
14	-1.730	"	43.9	38	+0.520	Iron active	
15	-1.768	"	None	Iron rendered passive and current lowered to 10 M. A.			
17	-1.771	"	18.7	40	-1.775	10 M. A.	
18	-1.730	"	43.9	41	-1.776	"	H press.
19	-1.730	"	43.9	44	-1.728	"	43.9
20	-1.730	"	43.9	48	-1.747	"	34.0
21	-1.768	"	None	50	-1.755	"	30.5
23	-1.730	"	43.9	51	-1.761	"	25.8
25	-1.748	"	30.5	53	-1.770	"	None
26	-1.760	"	25.8				

of potential was coincident with the application of the pressure and independent of the gas led to the suspicion that perhaps the phenomena were not characteristic of passive iron alone. To test this, potential determinations were made, under analogous conditions, on the following electrodes: an iron cathode, platinum anode and cathode, and a copper anode. Table VI shows the changes produced. The data for cathodes are only approximate, due to lack of constancy, so that the results are only qualitative, although the change with pressure is quite evident and it becomes clear that *on application of gaseous pressure, anodes, from which gas is being evolved, become more positive and cathodes more negative.* Nernst's equation for the potential of metal electrodes can be extended to the effects just described if the anode is considered as coated with an oxygen film or charged with oxygen, as by occlusion. In the equation $E = (RT/Fn) (\text{nat log } P/p)$, P would represent the solution tension of the oxygen which is associated with the metal, and p would represent the osmotic pressure of oxygen ions in the solution. The application of any external pressure would then immediately increase the concentration of the oxygen associated with the metal and thus raise the solution tension P and the value of E the potential. On the other hand, the increase of the value of the osmotic pressure p would be a slow process, so that on application of external pressure the value P increases faster than p and there results the rise in anode potential. Exactly analogous relations exist in the case of the cathode and a similar explanation of the increased negativity of cathodes can be made. From the form of

the factor ($\text{nat log } P/p$) it is to be expected that the change of potential with pressures, such as those used, would be small. Taking into consideration the facts indicating the presence of an oxygen film, this is the most useful hypothesis to apply in this case where the change in potential is small, such as would be expected if a gas film were considered. If occluded oxygen or an oxygen charge is assumed we are at loss for satisfactory explanation due to lack of knowledge of the coefficient of occlusion. The effects of pressure on potential, as above detailed, are new and merit fuller investigation. The potential measurements led directly to the studies which follow.

TABLE VI.

Platinum anode.			Iron cathode.		
0.2 N H ₂ SO ₄ , temp 0°.					
Polarizing current 8 M. A.					
Time in minutes.	E. M. F.	Hydrogen pressure. Lbs. per sq. in.	Time in minutes.	E. M. F.	Pressure. Lbs. per sq. in.
Start	-1.899	0	Start	+0.069	None
1	-1.898	0	4	+1.069	"
2	-1.879	50	7	+1.058	40 (hydrogen)
3	-1.882	40	9	+1.057	"
7	-1.884	38	10	+1.057	"
9	-1.885	35	15	+1.065	None
12	-1.890	28	20	+1.069	"
13	-1.898	0			
15	-1.898	28			
18	-1.893	34			
21	-1.886	46			
24	-1.882	57	Start	+1.680	None
26	-1.882	57	2	+1.680	"
27	-1.903	0	5	+0.685	"
			7	+0.673	43 (oxygen)
			8	+0.697	None
			10	+0.673	43 (oxygen)
			11	+0.676	43 "
			13	+0.793	None
Copper cathode.			Platinum cathode.		
Start	+1.141	None	Start	+1.680	None
2	+1.140	"	2	+1.680	"
4	+1.127	29 (oxygen)	5	+0.685	"
6	+1.050	41 "	7	+0.673	43 (oxygen)
7	+1.160	None	8	+0.697	None
			10	+0.673	43 (oxygen)
			11	+0.676	43 "
			13	+0.793	None

In the hope of obtaining a more intimate knowledge of the processes of passivation a study was made of the changes of the potential of iron while it was passing from the active to the passive state, and the reverse. The conditions and apparatus used were exactly the same as in the work just detailed. The field of polarization potentials is one of unusual difficulty, because an electrode in contact with an electrolyte shows great variation in behavior, especially when an external current is impressed. Using the potentiometer previously described, the changes in potential when the iron was used as an anode were found to be interesting, but when attempts were made to get accurate readings of the momen-

tary values it was found that satisfactory and reproducible values could not be obtained.

The potential behavior of iron in contact with 0.2 *N* sulfuric acid, when no external current is flowing, has been previously described, and, as was shown in Table I, the potential gradually became more positive on standing. This value does not attain constancy in the course of two hours. Different specimens of iron wire on immersion in the acid show potentials ranging from +0.506 to +0.522 volt. When the external current, 10 milliamperes was applied, the potential quickly became less positive and at the end of two seconds it had generally passed through the value +0.11 volt. (See Fig. 2.) Then the change became slower and there was a continuous fall to about -0.15, and this was soon followed

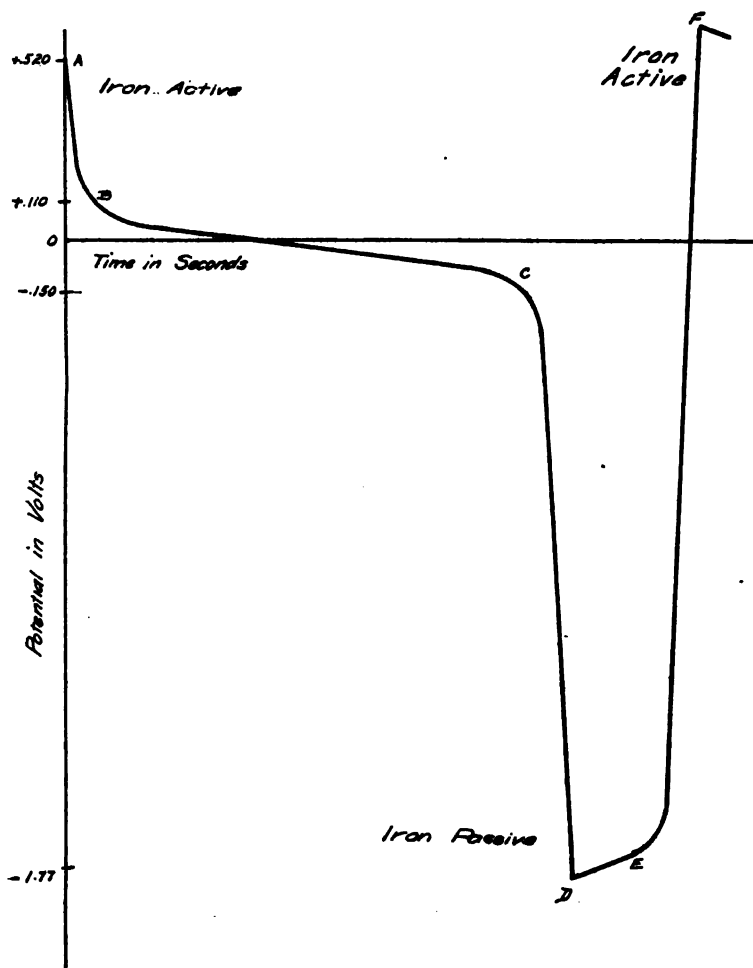


Fig. 2.

by a very rapid fall to the neighborhood of -1.85 . Coincident with this last sudden drop the iron became passive and the resistance at the anode surface increased, as was shown by the fall in polarizing current.

When the external current was stopped the potential did not change greatly for a little while and then there was a very sudden rise as the iron became active. The time elapsing before activation sets in is longer when the passive electrode has been polarized for a greater length of time or when a high current has been used. On becoming active, with no external current flowing, the potential usually rose to a value slightly above 0.6 volt, which is higher than the initial value on first immersing the iron in the electrolyte. Potentiometer readings could not be made in the ordinary way, since during the processes the values were constantly changing. The current through the external circuit was changing in an analogous manner and this tends to show that the change of potential is associated with a change in resistance at the electrode surface. The external resistance was so arranged that there was, as nearly as possible, a current of 10 milliamperes flowing during the period shown in the curve by the length B to C. Using these conditions the method adopted was to choose a time, for instance five seconds, after the external current was applied, and then attempt to get as good readings of the potential at this time as was possible. The potentiometer circuit was closed with the instrument set at the estimated potential, then by the vigor and direction of the galvanometer throw the setting was estimated and, after the iron had been rendered active again, another trial was made at the end of the fifth second. Thus a value was approached; but there was always the difficulty that the potential of any particular specimen of wire was always changing and different samples gave different values, so that exact quantitative results were impossible. However, the graph gives a very good idea of the trend of events and the failure to obtain concordant results is characteristic of work in this field. Heathcote,¹ attempted to obtain a similar set of values with even less success, although he arrived at a somewhat similar curve for the changes of potential as iron becomes passive. The form of the curve (see Fig. 2) is such that it presents rather strong evidence in favor of the idea that the establishment of passivity is the result of two processes. The first of these would consist of the formation of a layer of insoluble material such as ferrous oxide. This would not be, of necessity, a firmly adherent coating and might be pierced by holes or pores. Its initial formation would correspond to the part of the curve from A to B. The other process would be the establishment of a film of oxygen gas which would form a complete cover over the electrode. The transition between these two processes is represented by the slow drop in potential shown between B and C, after which the

¹ *J. Soc. Chem. Ind.*, 26, 899 (1907).

cover rapidly becomes complete and potential drops from C to D. In a similar way the curve indicates that activification is a single process or at best practically the simultaneous removal of both the oxygen and the oxide coats. This removal is exceptionally complete as is shown by the final maximum potential. This may also be due to the removal of the occluded gases.

That the variation of anode potential is associated with a change of resistance at the anode surface is confirmed by the change in the polarizing current as the iron becomes passive. The graph (see Fig. 3) shows that

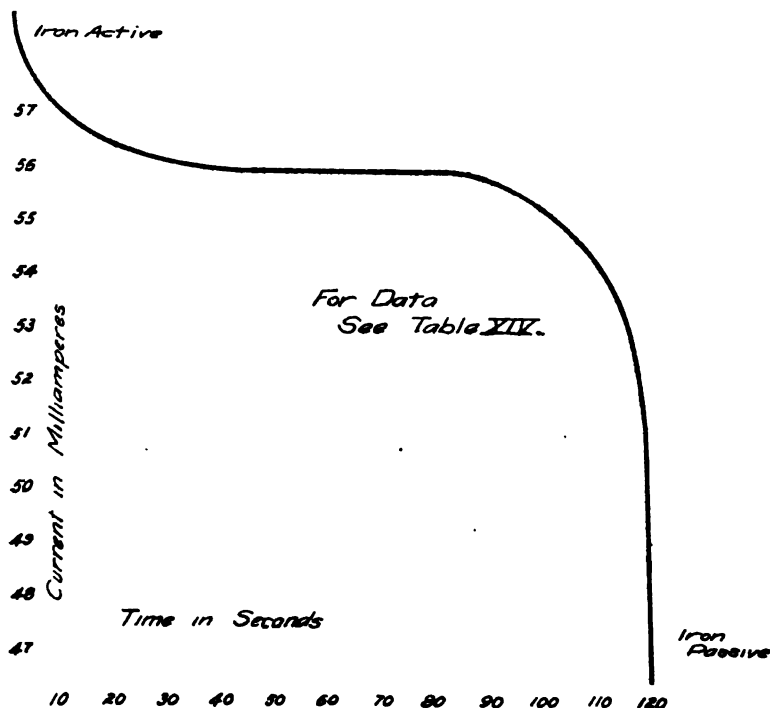


Fig. 3.

the variation in external current with time is exactly analogous to the changes in the anode potential during the process of passivification. In taking the data (Table VII) a long section of iron was used in order to obtain values of greater magnitude.

TABLE VII.

Conditions: Temperature, 18°. 0.2 N H_2SO_4 . Diameter of iron wire, 0.770 mm. 25 mm. wire exposed. The wire had previously been rendered passive two or three times. Several successive determinations on the same section of wire gave exactly similar results. Throughout the work the external resistance was not changed.

Time in seconds.....	0	3	10	17	32	75	85	95	105	110	117	120
Current milliamps.....	59	58	57	56½	56¼	56	56	55½	55	54	53	46½

The theoretical explanations of passivity are numerous and varied, but for the sake of brevity their historical review must be omitted, as well as the discussion of the principal phenomena.¹ However, in consideration of the seven factors mentioned at the opening of this paper, and in view of the potential relations above detailed, a brief theoretical statement now appears to be in order.

It seems to the authors that there is no general explanation of passivity but that the loss of activity is dependent upon the conditions, and that the explanation of the mechanism of the reaction will not come at one step by the announcement of an all-embracing hypothesis. Iron anodes in sulfuric acid behave differently, depending upon the circumstances. This has been pointed out by Schulze,² who says that in "dilute sulfuric acid iron shows passivity; in concentrated acid, valve action; in intermediate concentrations an unstable valve action succeeded by passivity." The nature of valve action is made clear by the behavior of aluminium, in that when used as an anode in a suitable electrolyte a film of aluminium oxide is formed and oxygen is evolved. The film is at first so thin that it is invisible but gradually builds up to a light gray coating pierced by very numerous holes of microscopic size. This film absorbs about 5% of the current, the rest being used in the formation of the oxygen which escapes. The work and conclusion of Schulze, although bearing largely on valve action, throw interesting and valuable light on the problem of passivity. The objection is often raised that, as in the case of iron, it is difficult to understand how oxide or hydroxide coatings exist in the presence of an acid electrolyte. Let us consider the case of a metal used as an anode and it is readily seen that there is no objection to the assumption that the surface of the metal itself is in contact with a neutral or alkaline medium, for since the anode is positively charged the hydrogen ions which bear a charge of like sign would be repelled, and their concentration materially reduced, in the zone of contact between the electrolyte and anode. On the other hand, negative ions would be attracted and increase the possibility of primary anionic discharge. The relations of iron to sulfuric acid are very complex, and it will be sufficient to outline the conclusions arrived at with respect to the mechanism of the establishment of passivity in iron when used as an anode in 0.2 *N* sulfuric acid, and under the *specific conditions* which have been maintained throughout the experimental work. There is little doubt but that we are concerned with surface conditions in our study of passivity. The potential curve shows that what occurs when passivity is established is a two-process change. The external current curve agrees with this.

¹ For a complete discussion see *Trans. Faraday Soc.*, 1914; Byers, *THIS JOURNAL*, 30, 1718 (1908); Heathcote, *J. Soc. Chem. Ind.*, 26, 899 (1907).

² *Trans. Faraday Soc.*, 1914.

Let us now consider a reaction mechanism that would account for these changes. (See Fig. 4.) The ordinary facts of electrode potentials show that metals can and do form ions directly so that with our iron anode it is very probable that there is an equilibrium between the metal and its ions. There is also evidence that the anions may be attracted to the surface of the anode and discharge directly on the iron to form free SO_4 radicals. These latter may react directly with the metal to form ferrous

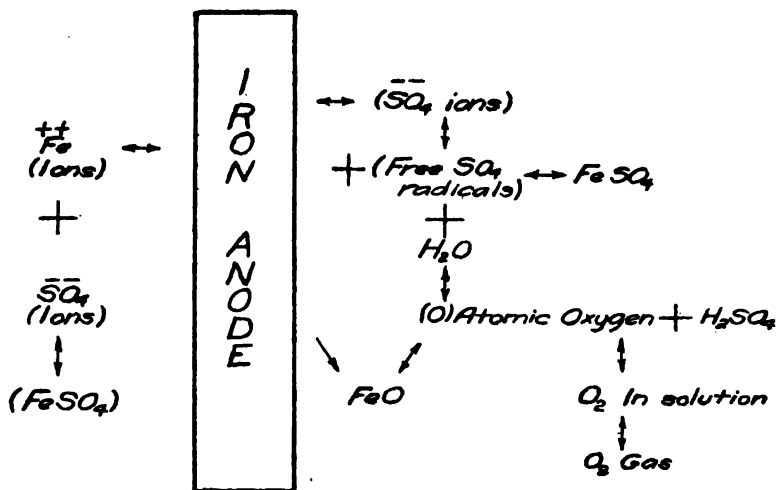


Fig. 4.

sulfate, or may react with water to form oxygen atoms. The oxygen atoms will react with the iron to form insoluble ferrous oxide or unite to form molecular oxygen. The equilibrium relations are shown diagrammatically in Fig. 4. Ferrous oxide is used in the equilibrium diagram to represent the initial step in the process of passivification, because this is the simplest assumption.

At the moment that the iron becomes an anode the greater part of the current is carried by means of iron ions entering the solution. But some anions are discharged directly on the surface of the iron and thus carry part of the current. These discharged ions can react with the iron to form ferrous sulfate, or with the water to form atomic oxygen, which in turn can form ferrous oxide or oxygen molecules. In the latter case the solution would eventually become saturated with oxygen and the gas would escape. But the formation of bubbles against an external pressure is a process that requires energy, and it seems that so long as the free iron is readily available it requires less work to form the very insoluble ferrous oxide. However, the more oxide that is formed the less free iron is available and more sulfate ions are primarily discharged, so that the concentration of free oxygen atoms would be so increased that the equi-

librium would be changed to the direction of the formation of oxygen molecules in solution. On saturation, if the intensity of the reaction is sufficient, gas will form and the electrode become covered with a film of oxygen, the high resistance of which accounts for the last final drop in the potential and current curves. On account of the surface tension this formation of the gas film will be quick and complete.

This hypothesis fits the facts which are characteristic of the behavior of passive iron anodes under the conditions studied. Particular attention is called to the strong confirmatory evidence given by the fact, established in the previous research, *that dissolved oxygen increases the speed with which passivity is established*, but does not materially affect the potential. With the high oxygen pressures the equilibrium conditions are made more favorable for the formation of the ferrous oxide and for the formation of the oxygen film. The fact that stirring retards the establishment of passivity is in perfect accord with the explanation given, for it certainly would tend to tear off the film of oxide, thus keeping fresh iron constantly exposed. However, after the passivity has been once established, the tendency of stirring to destroy the condition would be reduced to a minimum by the tendency of surface tension to keep the gas film intact. The re-establishment of activity occurs when, after the external current has been stopped, the gas film becomes ruptured in any way. Then the iron and oxide layers are in relation to each other very much as in a short-circuited cell and the activification occurs almost at once. The retarding influence of higher temperatures offers no difficulty. The fact that very low current densities do not passivify is not surprising in view of the equilibrium conditions which have to be established. It is here unnecessary to review all of the facts of passivity of iron to show that they accord with the explanation offered.

Summary.

The work previously done, in which seven critical factors bearing on passivity were established, has been extended to a study of the electro-motive behavior of polarized passive electrodes.

A special modified calomel cell for working at high pressures is described.

On application of gaseous pressures, anodes of passive iron, or any other metal anode from which oxygen was being evolved, became more electro-positive and cathodes more electronegative. The change was a function of the mechanical pressure and not of the degree of saturation of the electrolyte with dissolved gas.

Measurements of the variations of polarizing current and of anodic potential during the process of passivification gave curves which indicated that passivification was here a two-process operation.

It is pointed out that there is no one general explanation of passivity,

but rather that in each case, the loss of activity is dependent upon the conditions.

A theoretical explanation is offered for the conditions studied.

SEATTLE, WASHINGTON.

NOTE.

A Simple Bath Used for the Solution of Samples in an Oxygen-free Atmosphere.—The apparatus here described has for its application the solution of materials requiring heat in the absence of air. If a non-aqueous bath is desired it should be planned on smaller dimensions to avoid undue loss of liquid used.

An eight-inch porcelain evaporating dish is used for the bath. (See Fig. 1.) In the evaporating dish are placed some glass beads and a five-inch porcelain desiccator plate having under supports. On this plate is placed a heavy circular, square or triangular glass rod support for the dish which is to contain the sample. This support holds the dish in position. (A small porcelain desiccator plate can be inverted and used for the same purpose, the supports serving as points which partially enclose

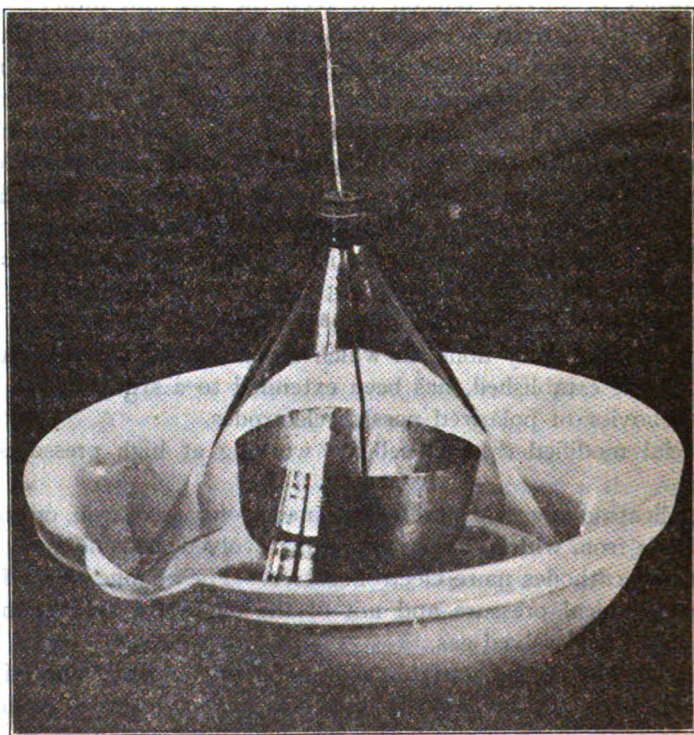


Fig. 1.

and support the dish.) Over the plate is inverted a six-inch funnel, with stem cut off, which extends down into the evaporating dish to a sufficient extent to form a trap when a liquid is poured into it. The liquid to be used is selected for the particular purpose at hand, *viz.*, water, a salt solution, an acid such as sulfuric acid or a nonaqueous solvent. Ordinarily the point to be considered is the adjustment of the atmosphere and temperature to suit the purpose of the experiment.

For the determination of ferrous iron in a silicate, a platinum dish is used as the inner container to hold the sample to be analyzed and a platinum rod is extended through the funnel into the dish. This rod is used for stirring and for the addition of hydrofluoric and sulfuric or hydrochloric acids. Phosphoric acid (1 : 2) is used as the solution to form a trap and also to furnish steam. Sufficient solution should be added to cause part of the platinum dish to be immersed. The advantage of phosphoric acid is that it elevates the boiling point of the water to such an extent that the solution contained in the platinum dish is heated much hotter than with water alone, also as more and more steam is evolved the phosphoric acid becomes more and more viscous, still forming a trap and evolving steam which keeps out the air, yet no crystallization occurs as in the case with many salt mixtures. The bath is heated by a direct flame or by an electric hot plate. Hot water, from which any dissolved gases have been removed by boiling, can be easily added to replenish the water lost by evaporation, a steady flow of steam being maintained without difficulty and a uniform heat obtained until the sample is thoroughly decomposed. However, with proper adjustment of volume of solution added at the beginning, and with proper intensity of boiling no addition of water is necessary during a heating period of an hour or even longer. After the sample is completely decomposed it is analyzed according to any reliable method for the determination of ferrous iron.¹ Air-free water should be used to dilute the solution and care should be exercised to avoid oxidation of the iron by the oxygen of the air.

This apparatus is simple, requires no accessories not available in any ordinary laboratory, and is easily adapted to particular temperatures by proper selection of boiling point mixtures.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]
THE OXIDATION OF ETHYL ALCOHOL BY MEANS OF POTASSIUM PERMANGANATE.

BY WILLIAM LLOYD EVANS AND JESSE E. DAY.

Received December 7, 1915.

During the early part of the latter half of the last century, it came to be recognized that the character of the oxidation products of both organic

¹ See Barnebey, *THIS JOURNAL*, 37, 1481, 1829 (1915).

and inorganic substances, with potassium permanganate as the oxidizing agent, was partially dependent upon whether the reaction took place in acid, neutral or alkaline media. Péan de Saint-Gilles¹ was among the first to observe this fact. In working with a number of organic compounds, he obtained varied products, the most common of which were formic, carbonic, acetic acids, etc. A few years later, Chapman and Smith² in their experiments on the action of an aqueous solution of potassium permanganate upon ethyl alcohol, found that small quantities of acetaldehyde, acetic and oxalic acids were formed, together with small quantities of other compounds. They furthermore found that, if the potassium permanganate solution was rendered strongly alkaline with potassium hydroxide, neither acetaldehyde nor acetic acid were produced. "If the solutions were used hot, oxalic acid was the principal product; if cold, various other acids, probably identical with those obtained by Debus in his oxidation of alcohol by nitric acid, were produced." It so happens that the work of these two men is nonreproducible as they incorporated no tangible data into their paper.

Since that time similar experiments with ethyl alcohol have been carried out by different investigators, the results of which are not in complete harmony with each other. With but one exception³ acetic acid has been found in every case. Chapman and Smith obtained oxalic acid as a reaction product when a neutral potassium permanganate solution was employed, while others found it only when using an alkaline solution of the permanganate. Voisenet⁴ detected traces of formaldehyde as another reaction product. According to the results of Fournier⁵ an acetic acid yield of about 50% of the theoretical amount is possible when a strongly alkaline solution of permanganate is employed. He obtained analogous results with propyl, butyl and isobutyl alcohols, when oxidizing them under similar conditions. In the case of ethyl alcohol he did not determine the character and amounts of the remaining 50% of the oxidation products, except to note that if acetaldehyde and ethereal salt were formed, they were in very small amounts. Recently, Denis⁶ carried out two experiments on the behavior of ethyl alcohol towards potassium permanganate, (1) in cold neutral aqueous solution and (2) in cold strongly alkaline aqueous solution. In the first instance she found acetic acid to be the sole reaction product. "When, however, potassium hydroxide was present in excess, acetic acid was still the principal product, but carbonic and oxalic acids were also formed—in larger amount the greater the concentration.

¹ *Compt. rend.*, 46, 808-11 (1858).

² *J. Chem. Soc.*, 20, 301-3 (1867).

³ Chapman and Smith, *Loc. cit.*

⁴ *Compt. rend.*, 150, 40-3 (1910).

⁵ *Ibid.*, 144, 331-3 (1907).

⁶ *Am. Chem. J.*, 38, 564 and 569-71 (1910).

of the caustic alkali used." In this connection, the recent observations of Witzemann¹ on the oxidation of glucose, are of great interest. In making a study of the action of neutral potassium permanganate towards ethyl alcohol, Morawsky and Stingl² obtained nothing but acetic acid. From their work on the effect of temperature, they concluded that increase in temperature merely promoted the rate of reaction.

Péan de Saint-Gilles³ believed that the temperature was also an important factor which might influence the character and amounts of the reaction products.

Hemmelmayer,⁴ in his work on the oxidation of sodium ethylate by the oxygen of the air at ordinary temperature, obtained an acid distillate on the distillation of the oxidation mixture with sulfuric acid. But at a temperature of 100°, a small amount of carbon dioxide was formed, and at 200°, traces of oxalic acid were evident as a product additional to the other two acids. The amounts of the two latter substances were considerably increased at 210°. The acid distillate, on analysis, proved to be composed of formic and acetic acids. His results with sodium ethylate have been verified by Nef.⁵

Hitherto, definitely chosen conditions have not been used in much of the experimental work on the oxidation of organic compounds by chemical substances. Among some of the exceptions to the above statement should be included the work of Heimrod and Levene⁶ on "Oxidation of Aldehydes in Alkaline Solution" and that of Kastle and Loevenhart on the "Oxidation of Formaldehyde by Hydrogen Peroxide."⁷ No complete systematic study has been made, from the standpoint of the effect of temperature and the concentration of alkali, on the character and relative amounts of the oxidation products formed when ethyl alcohol is oxidized by means of potassium permanganate in neutral and alkaline media. Nef⁸ records the fact that in the oxidation of many carbohydrates in alkaline solutions, the amount of lactic acid formed varies in a remarkable way, with the concentration of the caustic alkali used. In view of these facts, this work was undertaken with the intention of ascertaining the nature of the above-mentioned relationships. It is the aim, at present, to continue in this laboratory, a study, at given temperatures, of the oxidation of many organic compounds by means of potassium permanganate in the presence of varying concentrations of alkali.

¹ THIS JOURNAL, 38, 151-161 (1916).

² *J. prakt. Chem.*, 18, 82-3 (1878).

³ *Ann. chim. phys.*, [3] 55, 375 (1859).

⁴ *Monats. Chem.*, 12, 155-7 (1891).

⁵ *Ann.*, 318, 177 (1901).

⁶ *Biochem. Z.*, 29, 31-59 (1910).

⁷ THIS JOURNAL, 21, 262 (1899).

⁸ *Ann.*, 357, 215, compare *Ann.*, 357, 258 (1907).

Mr. H. B. Adkins is now engaged in a study of acetaldehyde under known conditions, with a view of correlating his results with these on ethyl alcohol.

Experimental Part.

Methods of Analysis.—Ordinary qualitative methods were employed in the detection of carbonic, acetic and oxalic acids. The presence or absence of formic acid was determined by using a modification of the Jones method on the neutralized acetic acid distillate, by making it alkaline with 1.0 g. of sodium carbonate and adding potassium permanganate solution of known strength until a pink color in moderately warm solution was obtained.¹

The quantitative determination of carbon dioxide was made by means of the Foulk² apparatus. A known portion of the solution under analysis was treated with the proper amount of hydrochloric acid and the carbon dioxide evolved, after having been conducted through a well-cooled condenser and the appropriate drying agents, was absorbed by a caustic potash solution. A correction was applied for the amount of carbon dioxide contained in the potassium hydroxide employed in the oxidations.

An aliquot part of the solution containing the oxidation products was employed in ascertaining the amount of oxalic acid present. The portion was first slightly acidulated with acetic acid, then made slightly alkaline with ammonium hydroxide, after which the soluble oxalate was converted to the insoluble oxalate by means of calcium acetate in hot solution. This precipitate, after being filtered and washed, was titrated against standard potassium permanganate solution in the presence of sulfuric acid in the usual manner.

The acetic acid was determined by the well-known method of Stilwell and Gladding as modified in this laboratory by Withrow and Fritz.³ A portion of the original solution, to which had been added an excess of sirupy phosphoric acid, was distilled in a vacuum apparatus. The distillate was titrated with a potassium hydroxide solution of known value, with phenolphthalein as the indicator. In each case a correction was made for the volatile acids contained in the amount of phosphoric acid used. It was observed in making these distillations, that when the amount of potassium hydroxide present was large, a much larger excess of the phosphoric acid, over that required for the neutralization of the alkali, was necessary in order to distill the last portions of the acetic acid.

Absolute alcohol was employed in this series of oxidations. It was dehydrated by means of calcium oxide and anhydrous copper sulfate in the customary way. Each liter of the standard solution contained 92.096 g. of the water free alcohol (b. p. = 77–77.5° C.), which was a 2 molar

¹ Compare: THIS JOURNAL, 34, 1091 (1912).

² Foulk, "Notes on Quantitative Chemical Analysis," p. 222, 1914 ed.

³ See thesis for M.A. by Howard Fritz, this laboratory.

or 9.21% solution. The specific gravity of the aqueous solution at 20° was 0.9847.

Each oxidation was carried out in the following manner: Thirty grams of crystallized potassium permanganate were placed in a wide-mouth, two liter balloon flask containing 1000 cc. of water which previously had been boiled free from carbon dioxide. In case of alkaline solutions, the desired amount of caustic potash (purified by alcohol) was then added. The flask was immediately closed by a rubber stopper into which was fitted a mechanical stirrer, a 25 cc. pipet and a piece of ordinary size glass tubing. The closed vessel was next clamped in position in a thermostat which was kept at 50°. When the temperature of the contents of the flask and that of the surrounding bath were at the desired value and while the mixture was in complete agitation, the alcohol solution (strength = 9.21%) was slowly admitted, drop by drop, until the reduction of the permanganate was complete. The determination of the end-point was made without difficulty by drawing a portion of the reaction mixture into the pipet, where, after the subsidence of the precipitated hydrated manganese dioxide, the observation could be made. In the majority of cases the end-point was passed to a slight extent, which made it necessary to add solid permanganate until a slight permanent color was attained which was generally discharged within twenty-four hours. The color desired in the case of alkaline solution was a very pale green and in the neutral solution was a delicate pink. The reaction mixture, after being filtered in a specially constructed carbon dioxide free apparatus, was made up to a volume of 2000 cc. and then analyzed.

The results obtained from a series of nine such oxidations can be observed in the tabular data and also as represented in the form of curves shown in Figs. 1 and 2. In Fig. 1 is the curve representing the number

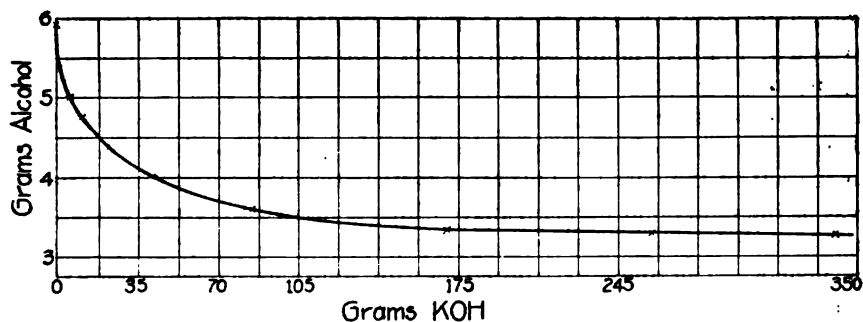


Fig. 1

of grams of absolute alcohol that is required to completely reduce a constant amount of potassium permanganate (30 g.) as the concentration of the alkali was increased. Beyond an alkalinity of about 175 g. per liter

of water, an increased amount of the potassium hydroxide had practically no further effect on the amount of alcohol necessary to bring about complete reduction. It becomes self-evident that the alcohol curve in reversed position would be the curve for variable permanganate with constant alcohol. The curves showing the amounts of the oxidation products in Fig. 2 were plotted on the latter basis, *i. e.*, a constant quantity

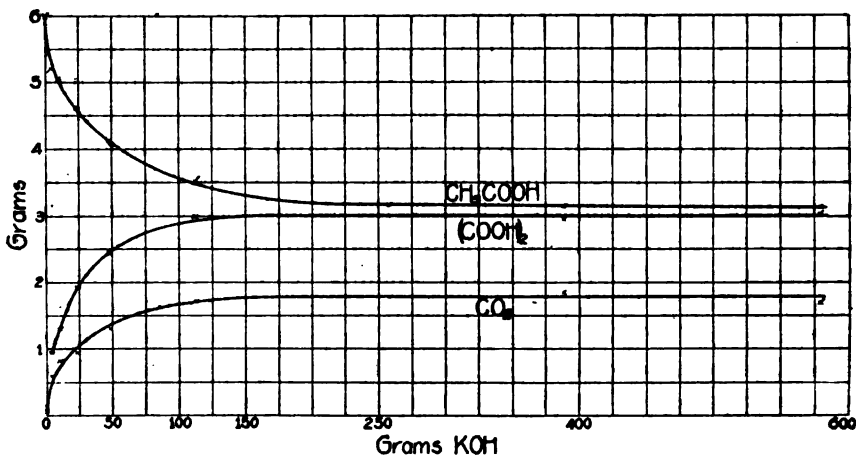


Fig. 2

of alcohol (5 g.). Such a course carried with it the necessity of proportionally increasing or decreasing the amount of potassium hydroxide actually used, depending upon whether the amount of alcohol required was greater or less than 5 g., so that the corresponding concentration of the alkali might be maintained. To be more explicit, take *e. g.*, the case of Expt. 4 where 4.37 g. of alcohol were actually oxidized. In order to oxidize 5 g. of alcohol it would have been necessary to increase the potassium permanganate to 34.3 g., the potassium hydroxide from 21.3 to 24.4 g. and the amount of water from 1000 to 1144 cc.

An error is introduced when the amount of potassium permanganate used is greater than 30 g. If the quantity of alcohol is less than 5 g., then the amount of alkali requisite for 5 g., as computed above, will lie to the left of the curve. This error systematically increases with the excess of the potassium permanganate which is needed to return to the end-point when it has been passed by the addition of a superfluous amount of alcohol. The above is true largely for solutions having values of alkalinity represented by any point in the bend of the curve.

It will be noticed in Fig. 2 that, in the case of the absence of added caustic potash, a small amount of carbonic acid was found. The lowest concentration of potassium hydroxide employed was 0.53% and at this value, oxalic acid was found in addition to the other products. At present we do not know from experiment, in the case of alcohol, the lowest exact

concentration of potassium hydroxide necessary for the formation of the latter named acid. For acetaldehyde, McLeod¹ has found that vinyl alcohol molecules are present in the aqueous solution of the aldehyde as soon as the concentration of the alkali is above 0.1%. In the case of alcohol, as the amount of potassium hydroxide was increased to about 250 g., the oxalic and carbonic acids simultaneously increased, although at different rates. Beyond this concentration of potassium hydroxide, the curves become practically straight lines, parallel to the X-axis. It required two drops of potassium permanganate solution (strength = 0.089 N) to give a slight permanent color to the distillate containing acetic acid when it had been previously made alkaline with sodium carbonate. This may be taken as an indication of a mere trace of either formic acid or formaldehyde or both. The total amount of alcohol recovered as oxidation products, in some instances, was slightly higher than that demanded by theory, but this was undoubtedly due to the absorption of slight amounts of carbon dioxide during the process of oxidation.

Series of experiments at 25° and 75° will be completed within a short time and it is hoped that an early report of the same will be made in THIS JOURNAL. We hope to present a discussion of our results at that time.

TABLE I.

Actually used (grams).			C ₂ H ₅ OH calc. for 30 g.			Actually found with proper correction for CO ₂ and CH ₃ COOH (grams).			Calc. for 5 g. alcohol (grams).		
KMnO ₄ .	KOH.	C ₂ H ₅ OH.	KMnO ₄ .	CO ₂ . Ave. of two.	(COOH) ₂ . Ave. of two.	CH ₃ COOH. Ave. of two.	KOH.	CO ₂ . Ave. of two.	(COOH) ₂ . Ave. of two.	CH ₃ COOH. Ave. of two.	
31.18	None	6.17	5.94	0.088	None	7.400	None	0.071	None	6.000	
30.00	5.3	5.02	5.02	0.632	0.975	5.228	5.3	0.629	0.951	5.207	
30.41	10.7	4.83	4.76	0.768	1.259	4.873	11.2	0.795	1.303	5.044	
30.00	21.3	4.37	4.37	0.828	1.700	4.042	24.4	0.947	1.959	4.624	
30.27	42.6	4.07	4.04	1.058	1.996	3.356	52.3	1.300	2.451	4.121	
30.30	83.2	3.65	3.61	1.269	2.195	2.564	112.1	1.737	3.000	3.512	
30.00	170.4	3.34	3.34	1.184	1.999	2.110	258.1	1.772	2.992	3.519	
31.97	255.6	3.51	3.29	1.307	2.077	2.198	388.4	1.863	2.959	3.131	
35.38	340.8	3.89	3.28	1.335	2.370	2.440	579.3	1.716	3.049	3.139	

COLUMBUS, O.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON AMINES. THE FORMATION OF SCHIFF BASES FROM β -PHENYLETHYLAMINE AND THEIR REDUCTION TO ALKYL DERIVATIVES OF THIS AMINE.

[FIFTH PAPER.]

BY NORMAN A. SHEPARD AND ARTHUR A. TICKNOR.

Received November 30, 1915.

While working in coöperation with Professor Treat B. Johnson on an investigation dealing with the relationship between chemical constitution

¹ *A. m. Chem. J.*, 37, 24 (1907).

and the therapeutic action of certain organic bases, the writers were assigned the problem of synthesizing several N-substituted derivatives of β -phenylethylamine. Certain aromatic representatives of this class of compounds were desired in order to compare their pharmacological activity with that of β -phenylethylamine (I) and its *p*-hydroxy derivative, namely, *p*-hydroxyphenylethylamine or *tyramine* (II).



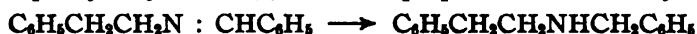
(I).



(II).

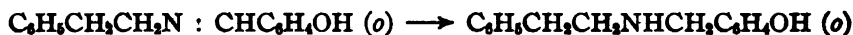
As is well known, both of these two bases (I and II) are physiologically active and, when injected subcutaneously, cause an increase in the blood pressure of the organism and also produce a strong contraction of the uterus.

We now give a description in this paper of the preparation and properties of five bases of this type, which have been incorporated in our work, namely: benzylphenylethylamine (IV), *p*-methoxybenzylphenylethylamine (X), *p*-hydroxybenzylphenylethylamine (VIII), *o*-hydroxybenzylphenylethylamine (VI), and 3-methoxy-4-hydroxybenzylphenylethylamine (XII). These were all prepared by reduction, with sodium and alcohol, of their corresponding Schiff bases, which were obtained by condensation of β -phenylethylamine (I) with the proper aromatic aldehyde.



(III).

(IV).



(V).

(VI).



(VII).

(VIII).



(IX).



(X).



(XI).



(XII).

Of these representatives of the two series, only (III), (IV) and (XI) have hitherto been described. Benzalphenylethylamine (III) was apparently first prepared by Walpole and Barger.¹ They gave, however, no description of its properties and assigned to it a melting point which we were unable to confirm. The Schiff base (XI) has been described by Decker and Becker,² and the alkyl amine benzylphenylethylamine (IV), was prepared by Fischer.³ The Schiff bases (III), (V), (VII),

¹ *J. Chem. Soc.*, 95, 1723 (1909).

² *Ann.*, 395, 367 (1913).

³ *Ber.*, 29, 211 (1896).

(IX) and (XI) were all solids and stable at high temperatures in the absence of water. The amines (III) and (IX) were distilled under diminished pressure without decomposition. The *p*-hydroxybenzal derivative (VII) was characterized by its high melting point (190°) which was 145° higher than that of the *o*-derivative (45°).

The transformations from the Schiff bases to the alkyl derivatives of phenylethylamine were nearly quantitative in the cases of benzylphenylethylamine (IV), *p*-methoxybenzylphenylethylamine (X) and *p*-hydroxybenzylphenylethylamine (VIII). The latter base is also formed quantitatively by heating its corresponding methyl ether with hydriodic acid. All three of these amines gave stable hydrochloric acid salts which were characterized by their crystalline character and insolubility in cold water. While *o*-hydroxybenzalphenylethylamine and 3-methoxy-4-hydroxyphenylethylamine undergo reduction with formation of their corresponding amines (VI) and (XII), respectively, the yields, however, were small because part of the Schiff bases underwent a normal hydrolysis with formation of β -phenylethylamine and the corresponding aldehyde.

Experimental Part.

Benzal- β -phenylethylamine, $C_6H_5CH_2CH_2N : CHC_6H_5$.—Barger and Walpole¹ prepared this substance by condensation of benzaldehyde with phenylethylamine. The compound was not analyzed by them, but they state that it melts at about 70° and on nitration is transformed into *p*-nitrophenylethylamine, $NO_2C_6H_4CH_2CH_2NH_2$. We have prepared the compound by the same method and find that it is easily purified by distillation under diminished pressure. Our base boiled at $188-189^{\circ}$ at 17–19 mm. pressure and, on cooling, solidified in the form of stout, colorless prisms which melted sharply at $41-42^{\circ}$. The yield of purified material was 91% of the theoretical.

Calc. for $C_{12}H_{14}N$: N, 6.70. Found: N, 6.8.

Benzyl- β -phenylethylamine, $C_6H_5CH_2CH_2NH.CH_2C_6H_5$.—This base has been described by Fischer¹ and was prepared by two methods. It was obtained from benzylphenylhydroxyethylamine, $C_6H_5CH_2NH.CH_2.CHOH.C_6H_5$ by reduction with hydriodic acid and phosphonium iodide, and also by reduction of the Schiff base, phenylethylidenebenzylamine, $C_6H_5CH_2N : CH.CH_2C_6H_5$, with sodium and alcohol. The yield by the latter method was 25% of the theoretical. We find that practically a quantitative yield of the same base is obtained by reduction of the above benzal derivative with sodium and alcohol. Our procedure was to dissolve 15 g. of the unsaturated compound in 300 g. of absolute alcohol and then reduce the double bond by slowly introducing 40 g. of metallic sodium. After the sodium had dissolved the alcohol solution was carefully diluted with water and finally acidified strongly with hydrochloric acid. On

¹ *Loc. cit.*

evaporating this solution the base was obtained in the form of its difficultly soluble hydrochloric acid salt. This crystallized from hot water in the form of glistening plates, which melted at $265-266^{\circ}$ to a clear oil (Fischer assigned $264-266^{\circ}$ as the melting point). From 15 g. of the Schiff base we obtained 18 g. of the hydrochloride.

***p*-Methoxybenzal- β -phenylethylamine**, $C_6H_5CH_2CH_2N:CHC_6H_4.OCH_3$.—This compound is easily obtained by condensation of anisic aldehyde with phenylethylamine. From 8.1 g. of the amine we obtained 13 g. of the unsaturated compound boiling at $224-225^{\circ}$ at 17 mm. pressure. This oil solidified on cooling to a colorless crystalline mass which melted at $34-35^{\circ}$ to an oil.

Calc. for $C_{16}H_{17}ON$: N, 5.85. Found: N, 5.77.

***p*-Methoxybenzyl- β -phenylethylamine**, $C_6H_5CH_2CH_2NHCH_2C_6H_4.OCH_3$.—Working under similar conditions as were employed for the preparation of benzylphenylethylamine from benzalphenylethylamine, we were successful in reducing the above *p*-methoxybenzalphenylethylamine to this base by the action of sodium and alcohol. It was obtained in the form of its hydrochloride which crystallized from hot water in the form of plates. They melted at $266-267^{\circ}$ to a clear oil without effervescence. The yield was excellent.

Calc. for $C_{18}H_{19}ON.HCl$: N, 5.04. Found: N, 4.94.

The free base is obtained as a colorless oil insoluble in water when the above salt is decomposed with alkali.

***p*-Hydroxybenzal- β -phenylethylamine**, $C_6H_5CH_2CH_2N:CHC_6H_4.OH$.—*p*-Hydroxybenzaldehyde condenses smoothly with phenylethylamine at 100° forming this unsaturated derivative. It was obtained in the form of deep yellow crystals which separated from 95% alcohol in yellow prisms. They melted at $188-190^{\circ}$ to a clear oil. The base is readily soluble in alcohol and difficultly soluble in benzene, from which it deposits in clusters or burrs of light yellow prisms. The yield of purified material was 83.0% of the theoretical.

Calc. for $C_{16}H_{15}ON$: N, 6.22. Found: N, 6.30.

***p*-Hydroxybenzyl- β -phenylethylamine**, $C_6H_5CH_2CH_2NH.CH_2C_6H_4.OH$.—*p*-Hydroxybenzalphenylethylamine is reduced smoothly by sodium and alcohol using the same proportions as previously given. The residue obtained, after the reaction mixture was acidified with hydrochloric acid and the solution evaporated, was treated with just enough water to dissolve the sodium chloride and leave the hydrochloride of the base undissolved. This salt was then separated and purified by crystallization from dilute hydrochloric acid, in which it was quite difficultly soluble. On cooling, it separated in leaflets which melted at $225-226^{\circ}$ to a clear oil. The compound was purified for analysis by recrystallization from

50% alcohol and separated, on cooling, as clusters of long prisms. The yield of purified material was 4.9 g. or 64.5 % of the theoretical.

Calc. for $C_{11}H_{11}ONCl$: N, 5.3. Found: N, 5.5.

The free base was obtained by decomposing the hydrochloride with ammonia. It separated in a crystalline condition and crystallized from alcohol in hexagonal tables which melted at $135-136^{\circ}$ to a clear oil. The amine was moderately soluble in ether and difficultly soluble in benzene. Nitrogen determinations in the free base after drying over concentrated sulfuric acid:

Calc. for $C_{11}H_{11}ON$: N, 6.17. Found: N, 6.2, 6.3.

This same amine was also formed by heating *p*-methoxybenzyl- β -phenylethylamine with hydriodic acid. Four grams of the methoxy compound were suspended in 35 cc. of hydriodic acid and the mixture boiled for one hour. Methyl iodide was evolved and a clear solution was obtained. On adding water to the hydriodic acid solution the hydriodide separated in the form of plates. The free base was obtained by treatment of this salt with ammonia and crystallized from alcohol as hexagonal prisms or tables melting at $135-136^{\circ}$. This base dissolves in sodium hydroxide solution and responds to Millon's test for a phenol group. An attempt to prepare the hydroxy base by heating *p*-methoxybenzyl- β -phenylethylamine with hydrochloric acid was unsuccessful. For example, the ether was recovered unaltered after heating with concentrated hydrochloric acid for 2 hours at $130-145^{\circ}$.

o-Hydroxybenzal- β -phenylethylamine, $C_6H_5CH_2CH_2N:CH.C_6H_4.OH$.—Eight grams of salicylic aldehyde were mixed with an equivalent weight of phenylethylamine at ordinary temperature. On standing there was an energetic reaction, with evolution of heat and formation of water. After heating at 100° for one hour to complete the reaction, this condensation product was obtained as an oil, which solidified on cooling. It was purified for analysis by recrystallization from hot alcohol and separated on cooling in the form of yellow prisms melting at 45.5° to a clear oil. The compound is very soluble in ether. The yield was practically quantitative.

Calc. for $C_{15}H_{15}ON$: N, 6.2. Found: N, 6.2, 6.17.

o-Hydroxybenzyl- β -phenylethylamine, $C_6H_5CH_2CH_2NH.CH_2C_6H_4.OH$.—Fifteen grams of the preceding condensation product, dissolved in 20 parts of absolute alcohol, were reduced at the boiling temperature of the alcohol with 2.5 parts of sodium. After the sodium had completely dissolved, the nearly colorless solution was cooled, diluted with water and then combined with 300 cc. of dilute hydrochloric acid (1 part water to 1 part concentrated acid). On evaporating to dryness at 100° a brown oil, soluble in alcohol and insoluble in ether, separated and was removed mechanically from a crystalline residue. This crystalline product, which

was identified as the hydrochloride of the above amine (2.7 g.) mixed with sodium chloride, was triturated with cold water to remove the sodium salt and then purified as follows: The free base was first liberated from its salt by treatment with ammonia and finally extracted with ether. On saturating this ether solution with hydrochloric acid gas the salt deposited at once as stout prisms or blocks. These melted at 130° to a clear oil. The salt is easily dissociated by heating and also when warmed with water. Nitrogen determination after drying to constant weight at 97° :

Calc. for $C_{12}H_{15}ONCl$: N, 5.3. Found: N, 5.6.

From the aqueous solution above, containing the sodium chloride, we recovered 2.5 g. of phenylethylamine, which was formed by hydrolysis of the unreduced Schiff base. When alcohol containing 1–2% of water was used as the solvent, practically no reduction took place by addition of sodium and phenylethylamine was the only base obtained.

3-Methoxy-4-hydroxybenzal- β -phenylethylamine, $C_6H_5CH_2CH_2N:-CHC_6H_3(OCH_3)(OH)$.—This base was prepared by condensing vanillin with phenylethylamine according to the directions of Decker and Becker.¹ In crystalline form, however, and also color and melting point our product did not agree with the description given by these investigators. Our compound separated from alcohol as stout, yellow columns or prisms which melted at $112-113^{\circ}$ to a clear oil, and the compound retained its yellow color after repeated crystallizations. Decker and Becker state that their product crystallized in colorless plates which melted at $108-109^{\circ}$.

Calc. for $C_{16}H_{17}O_2N$: N, 5.50. Found: N, 5.6, 5.7.

From the alcoholic filtrates left after crystallization of the above compound a small amount (0.3 g.) of a dark red, crystalline substance was obtained, which deposited from hot alcohol in rectangular plates. The color was not removed by repeated crystallizations from alcohol and benzene. The compound melted at $220-221^{\circ}$ to a red oil. It was practically insoluble in hot water, sodium hydroxide solution and hydrochloric acid and difficultly soluble in alcohol and benzene. This product, which contained 8.57% of nitrogen, was not examined further. This same substance was also formed during the condensation of *p*-hydroxybenzaldehyde with β -phenylethylamine. The quantity obtained, however, was very small (less than 0.5 g.).

3-Methoxy-4-hydroxybenzyl- β -phenylethylamine, $C_6H_5CH_2CH_2NH.-CH_2C_6H_3(OCH_3)(OH)$.—When 7.2 g. of 3-methoxy-4-hydroxybenzal- β -phenylethylamine were reduced with sodium and alcohol and treated in a similar manner as described under the preparation of *o*-hydroxybenzyl- β -phenylethylamine, 3.9 g., or 47% of the theoretical quantity, of the

¹ *Loc. cit.*

hydrochloride of the above base were obtained. This salt crystallized from dilute hydrochloric acid as clusters of slender needles, which melted at 180° to a colorless oil.

Calc. for $C_{16}H_{20}ONCl$: N, 4.78. Found: N, 4.73, 4.49.

In order to obtain the free base the hydrochloride was decomposed by ammonia and the amine extracted with ether. After drying the ether solution over sodium sulfate the solvent was then evaporated, when the amine was obtained as a solid. It crystallized from 95% alcohol in the form of needles and melted at $99-100^{\circ}$ to a clear oil. It was dried for analysis over concentrated sulfuric acid.

Calc. for $C_{16}H_{19}O_2N$: N, 4.34. Found: N, 4.5, 4.6.

Part of the Schiff base underwent hydrolysis during the above operation and we recovered 1.2 g. of the hydrochloride of phenylethylamine.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA.]

A NEW CASE OF TAUTOMERISM: 1,4,5,6-TETRAHYDROXY-NAPHTHALENE.¹

BY A. S. WHEELER AND V. C. EDWARDS.

Received December 20, 1915.

Zincke and Schmidt² reduced 5,6-dihydroxy- α -naphthoquinone (naphthazarine) with stannous chloride, obtaining a yellow compound, melting at 154° , which they designated 1,4,5,6-tetraoxynaphthalin. Its phenolic character was indicated by the easy preparation of a tetracetyl derivative, colorless prisms melting at $277-9^{\circ}$ with decomposition, and also by the fact that its solutions show a strong greenish fluorescence. A peculiar behavior of the solutions was noted in that they soon turn red if exposed to the air and deposit red crystals, which melt at the same temperature as the yellow compound, 154° . The deep color is retained after recrystallization. Heating and the presence of oxidizing agents hasten the change from yellow to red, but ultimate analysis indicates no change in composition and the two forms yield the same derivatives. The authors attributed the color to the presence of a highly colored oxidation product in slight amount. This peculiarity and the results obtained by Willstätter and Wheeler³ on the hydrojuglones led to the study of this phenol.

The Badische Anilin u. Soda-Fabrik, Ludwigshafen am Rhein, gener-

¹ This paper forms Part I of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of North Carolina by V. C. Edwards. Part II on The Bromination of 1,4,5,6-Tetrahydroxynaphthalene will appear later.

² *Ann.*, 286, 27 (1895).

³ *Ber.*, 47, 2796 (1914).

ously supplied the naphthazarine required for this research and we take this opportunity to express to them our sincere gratitude.

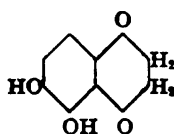
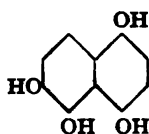
Willstätter and Wheeler reduced juglone and obtained α -hydrojuglone, a trihydroxynaphthalene of grayish green color, which readily passed on melting into the ketone form, a yellow compound, which had been regarded by Mylius¹ as another trihydroxynaphthalene, a theory which involves the migration of an hydroxyl group. The discovery of the ketone character of the β -hydrojuglone suggested the possibility that the tetrahydroxynaphthalene might also exist in two forms and our study of the compound shows that this is the case. We treated the tetrahydroxynaphthalene with the important ketone reagents, hydroxylamine, semicarbazine, phenylsemicarbazine, and several others not so often used. No oxime could be obtained, only a black amorphous product. The phenols of the naphthalene series are very sensitive to alkalis and our study shows that hydroxylamine is too basic. Semicarbazine, which is less basic, gave a crystalline product mixed with some amorphous material which, however, we were unable to remove. Phenylsemicarbazine, containing the added negative phenyl group, gave readily a pure crystalline phenylsemicarbazone. Other ketone reagents containing negative groups, as *p*-bromophenylsemicarbazine, *p*-nitrophenylsemicarbazine, benzhydrazine and *p*-nitrobenzhydrazine gave equally fine yellow crystalline products which were readily obtained in pure condition.

If we regard the hydrogens which were introduced by the reduction of naphthazarine as the more mobile ones, then there is the possibility of the presence of two ketone groups. This idea did not occur to Willstätter and Wheeler in their study of the hydrojuglones. By employing two molecules of phenylsemicarbazine we obtained a compound, the yield of which was 98% of the theoretical for a diphenylsemicarbazone. We have, however, been unable to obtain it perfectly pure. We made numerous attempts to methylate the tetrahydroxynaphthalene. Gummy or amorphous products were obtained with dimethylsulfate and also with diazomethane in ether solution but a chloroform solution gave a crystalline product. Methyl alcohol and sulfuric acid gave a derivative which, though it had no sharp melting point, gave good figures for a monomethyl ether. We were unable to prepare any metallic derivatives of tetrahydroxynaphthalene.

The tautomerism of 1,4,5,6-tetrahydroxynaphthalene differs from that of the hydrojuglones which are very easily obtained pure in the enol and keto forms. We tried many methods of conversion from enol to keto and of keto to enol forms but nothing has come under our notice except the yellow compound which melts at 154° and the red melting at the same point. All endeavors to distinguish any difference in behavior of

¹ Ber., 18, 478, 2571 (1885).

the yellow and red forms proved unavailing. Of these experiments one was a comparison of the speed of reaction of the two forms in alcoholic solution with phenylsemicarbazine. In both cases the carbazone began to appear at the end of six hours and the two reactions gave like yields. The development of the red color is largely prevented by substituting nitrogen for air. A slight amount of stannous chloride will also prevent the assumption of the red color. Single red crystals appear yellow under the microscope. A mass of crystals viewed directly is dark red and so are the solutions. Our conclusion is that the form of tautomerism here is like that of phloroglucinol where we are able to lay the finger upon one form only which reacts readily with both phenol and ketone reagents. Previous investigators have regarded the compound only as a phenol. We may represent the formulas as follows:



Experimental.

Purification of Naphthazarine.—The naphthazarine as obtained from the Badische Anilin u. Soda-Fabrik was not pure and a study of its purification was undertaken by Mr. V. C. Coulter in this laboratory. The purity of the product of each experiment was qualitatively tested by reducing a pinch with stannous chloride and hydrochloric acid. If the product was a clear yellow, it was comparatively pure. If it was greenish or blackish, it indicated an unsatisfactory method of purification. All of the well-known organic solvents and numerous mixtures of these were unavailing. Solution in alkali and reprecipitation with acid also proved unsatisfactory. Sublimation in an atmosphere of carbon dioxide at 230–40° gave a pure product but a small yield. Finally sublimation *in vacuo* in an electrically heated apparatus was resorted to with success. The apparatus of Morey¹ suggested to us the best arrangement. An abandoned base of an old style vacuum pump served perfectly for the bottom piece. A second inverted glass cylinder set within the crystallizing dish reduced the area upon which the naphthazarine condensed. A platinum dish was used to hold the substance. The heating element was made by winding nichrome wire around a plate of asbestos. A vacuum of 2–10 mm. was maintained and a current of 1.5 amperes was required. Each charge of 20 g. was sublimed in about eight hours. The yield of pure naphthazarine was 70% or over.

Reduction of Naphthazarine.—The use of alcohol as employed by Zincke and Schmidt was abandoned when it was found that a purer product

¹ THIS JOURNAL, 34, 550 (1912).

could be obtained with hydrochloric acid alone. Twenty grams of sublimed naphthazarine were boiled 20 minutes in 5 liters of 12% hydrochloric acid with the addition of 100 g. of stannous chloride. The light yellow solution was filtered hot with suction and allowed to cool down. About 18 g. of tetrahydroxynaphthalene crystallized out in plates or prisms which melted at $153-4^{\circ}$. Recrystallization was unnecessary.

Attempt to Prepare the Oxime.—Two-tenths of a gram of tetrahydroxynaphthalene, 0.075 g. of hydroxylaminehydrochloride and 0.10 g. of barium carbonate were heated with 15 cc. of absolute alcohol for four hours, and then allowed to stand for four days. No crystalline product could be isolated from the black amorphous precipitate or from the solution.

Semicarbazone, $C_{11}H_{11}O_4N_3$.—One gram of tetrahydroxynaphthalene was dissolved in 100 cc. of absolute alcohol and to this was added 0.57 g. of semicarbazine hydrochloride and 0.51 g. of potassium acetate in 3 cc. of water. The solution was kept in a stoppered flask. Crystallization began in four hours and was complete in a day when 1.05 g. of yellow crystals were filtered off. When heated these gave off violet vapors at $170-200^{\circ}$, becoming a soft, black mass. The product, consisting of yellow prisms, was insoluble in water and ligroin and only slightly soluble in other cold solvents. The solubility was only slightly increased in hot solvents. In all cases the microscope revealed a little amorphous material. The three samples analyzed were purified by extracting the impurities so far as possible with large quantities of solvents. I. 1.0 g. was shaken 24 hours with 500 cc. of methyl alcohol. II. 1.1 g. were shaken with 1 liter of ether and then with 500 cc. of methyl alcohol, each 24 hours. III. A portion of II was then shaken with 500 cc. of benzene and finally with 500 cc. of carbon tetrachloride, each 24 hours.

Calc. for $C_{11}H_{11}O_4N_3$: N, 16.85. Found: I, 18.50; II, 17.67; III, 17.01.

Phenylsemicarbazone, $C_{17}H_{15}O_4N_3$.—Two grams of the tetrahydroxynaphthalene were dissolved in 200 cc. of absolute alcohol and mixed with 1.6 g. of phenylsemicarbazine dissolved in 50 cc. of absolute alcohol. The solution was kept in a stoppered flask. In six hours clusters of yellow crystals began to form and after 24 hours 2.7 g. of product were filtered off. It crystallized from absolute alcohol in fan-shaped groups of short, stout needles, which melted at 218° with decomposition, giving off violet vapors.

0.1840 g. subst. gave 0.4128 g. CO_2 and 0.0826 g. H_2O ; 0.1570 g. subst. gave 17.54 cc. N_2 (18° and 757.5 mm. over 40% KOH).

Calc. for $C_{17}H_{15}O_4N_3$: C, 62.74; H, 4.65; N, 12.93. Found: C, 62.40; H, 5.12; N, 12.87.

To see if the reaction with phenylsemicarbazine would give any hint as to whether the yellow and red forms of the tetrahydroxynaphthalene represented enol and keto forms, comparative reactions were run both in

alcohol and chloroform solutions. In the alcohol solutions the phenylsemicarbazone appeared in six hours and in like amount when the reaction was complete. In the chloroform solutions the results were the same, except that the crystallization began in four hours. Thus no hint was obtained.

The phenylsemicarbazone is easily soluble in acetone, xylene and pyridine, much less soluble in alcohol, chloroform and benzene and insoluble in the other ordinary solvents. It was recrystallized from alcohol or chloroform.

Diphenylsemicarbazone.—In view of the reduction of two quinone oxygens, there should be two labile hydrogen atoms and hence the possibility of a diphenylsemicarbazone. One-half gram (1 mol.) of the tetrahydroxynaphthalene and 0.8 g. (2 mols.) of phenylsemicarbazine were dissolved in 70 cc. of absolute alcohol and set aside in a stoppered flask. Crystallization began in about 3 hours and after 3 days 1.17 g. of product, consisting of yellow prisms, were filtered off. The crystals were very slightly soluble in acetone, ethyl and amyl alcohols and practically insoluble in other organic solvents. Acetone extracted a small quantity of a compound consisting of scales and melting at $120-1^{\circ}$. The insoluble crystals consisted of hexagonal plates which darkened at 280° and at $285-7^{\circ}$ a dark liquid condensed on the upper walls of the capillary tube.

0.1621 g. subst. gave 25 cc. N_2 (26° and 752 mm. over 40% KOH). Calc. for $C_{16}H_{12}O_4N_2$: N, 18.34. Found: 17.04.

We were unable to obtain a purer compound. The war shut off our supply of naphthazarine and hence this investigation is temporarily interrupted.

***p*-Bromophenylsemicarbazone, $C_{17}H_{14}O_4N_2Br$.**—Two grams of tetrahydroxynaphthalene, dissolved in 200 cc. of alcohol, were mixed with 2.4 g. of *p*-bromophenylsemicarbazine in 250 cc. of alcohol. In 7 hours no reaction was apparent but in 8 days a product weighing 1.47 g. was obtained. It was insoluble in water and ligroin but soluble in alcohol, ether, benzene, chloroform and carbon tetrachloride. It crystallizes from hot acetone in yellow needles which decompose at $220-3^{\circ}$.

0.0688 g. subst. gave 0.0416 g. AgBr. Calc. for $C_{17}H_{14}O_4N_2Br$: Br, 19.97. Found: 19.54.

***p*-Nitrophenylsemicarbazone, $C_{16}H_{13}O_5N_3$.**—One and one-half grams of tetrahydroxynaphthalene and 1.2 g. of *p*-nitrophenylsemicarbazine were dissolved in 200 cc. of absolute alcohol and set aside in a stoppered flask. After 6 hours crystallization began and after 40 hours 1.23 g. of greenish yellow crystals were filtered off. The product was not readily soluble in alcohol, ether or benzene. It crystallized from hot acetone in yellow needles or prisms which began to decompose at 234° and at about 241° gave off violet vapors.

0.0871 g. subst. gave 9.90 cc. N_2 (17° and 748 mm. over 40% KOH). Calc. for $C_{16}H_{14}O_4N_2$: N, 12.85. Found: 12.98.

Benzhydrazone, $C_{17}H_{14}O_4N_2$.—One-half gram of tetrahydroxynaphthalene in 50 cc. of alcohol was added to 0.4 g. of benzhydrazine in 10 cc. of alcohol. No crystals appeared on the first day but after 4 days 0.51 g. of product was obtained. It was fairly soluble in acetone and alcohol, less so in ether and benzene and insoluble in water. It was purified by dissolving in acetone and pouring the solution into water. The pure substance consisted of beautiful yellow needles which decomposed between 170 and 185° .

0.1087 g. subst. gave 8.85 cc. N_2 (19° and 743.8 mm. over 40% KOH). Calc. for $C_{17}H_{14}O_4N_2$: N, 9.04. Found: 9.17.

***p*-Nitrobenzhydrazone**, $C_{17}H_{12}O_6N_2$.—One-half gram of tetrahydroxynaphthalene and 0.5 g. of *p*-nitrobenzhydrazine were dissolved in 100 cc. of alcohol, warmed for 4 hours and set aside for 2 days. Dark yellow crystals, weighing 0.2 g., were filtered off and from the mother liquor a further quantity was obtained on concentration. These crystallized from acetone in yellow needles which melted at $220-4^\circ$ with decomposition.

0.0922 g. subst. gave 9.70 cc. N_2 (23° and 744 mm. over 40% KOH). Calc. for $C_{17}H_{12}O_6N_2$: N, 11.83. Found: 11.65.

Action of Dimethylsulfate.—One gram of the tetrahydroxynaphthalene was dissolved in 10% sodium hydroxide and to this was added 2.6 g. of dimethylsulfate. After 40 hours the reaction was examined. The precipitate consisted of dark amorphous material which yielded no crystalline product to any solvent. The reaction was repeated with twice the amount of dimethylsulfate. A few crystals were noted in much amorphous material.

Action of Diazomethane.—Four-tenths of a gram of tetrahydroxynaphthalene were dissolved in ether and treated with a slow current of ether and diazomethane vapors. After an hour some ether solution of diazomethane was added and the mixture was set aside for two days. The solution had become reddish yellow. When it was concentrated *in vacuo* only a black gummy mass was left. A chloroform solution gave better results. 0.2 g. of tetrahydroxynaphthalene was dissolved in dry chloroform and 0.2 g. of diazomethane was passed in slowly. This was practically all absorbed. After a week the chloroform was evaporated off and fan-shaped groups of crystals were obtained but some amorphous material was present. The product weighed 0.18 g. It was almost completely soluble in alcohol or chloroform but was unfortunately lost through an accident. It is hoped to study this reaction again.

Action of Methyl Alcohol in Sulfuric Acid.—1.5 g. of tetrahydroxynaphthalene were dissolved in 500 cc. of absolute methyl alcohol and 15 cc. of conc. sulfuric acid. The mixture was boiled 75 min. under a re-

flux condenser using a half atmosphere of excess pressure. The reaction mixture was poured into 150 cc. of hot water, boiled and filtered from a slight residue. The reddish filtrate upon cooling gave a large crop of reddish yellow needles which after twice recrystallizing from hot water gradually melted between 115 and 140°.

0.1659 g. subst. gave 0.4976 g. CO₂ and 0.0784 g. H₂O. Calc. for C₁₂H₁₀O₄: C, 64.08; H, 4.85. Found: 64.05, 5.32.

The analysis indicates a monomethyl ether but we believe the reaction will bear further study.

Metallic Salts.—Attempts were made to prepare metallic salts of the tetrahydroxynaphthalene. Water and alcohol solutions were used but no salts of barium, lead or silver could be obtained.

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[CONTRIBUTION FROM THE UNIVERSITY OF PITTSBURG, DEPARTMENT OF CHEMICAL ENGINEERING.]

THE PRESENCE OF BENZENE HOMOLOGS IN THE HIGH BOILING DISTILLATES OF PETROLEUM.

BY BENJAMIN T. BROOKS AND IRWIN W. HUMPHREY.

Received December 14, 1915.

In studying the properties of the substances which cause fluorescence in petroleum distillates,¹ the conclusion was drawn that the substances in question were probably related to benzene and the essential facts advanced in support of this hypothesis were the following:

(1) Oils distilled *in vacuo* are much less fluorescent than when distilled slowly at ordinary pressure and accompanied by cracking and formation of relatively large quantities of coke. There is an unmistakable parallelism between the distillation of coal *in vacuo* and at atmospheric pressure and the distillation of oil under similar conditions. In general, destructive distillation of organic material containing little oxygen is conducive to the formation of aromatic hydrocarbons. The coal-tar distillates produced by distillation *in vacuo* are relatively very low in aromatic hydrocarbons and are only very slightly fluorescent.²

(2) No fluorescent organic substances are known which belong strictly to the paraffin or naphthene series of hydrocarbons. The vast majority of fluorescent organic compounds, whose constitution is known, possess condensed ring structures such as the derivatives of benzene, naphthalene, anthracene, fluorene, pyrone, acridine, azine, oxazine, thiazine, and the like. The character of the fluorescence of petroleum distillates is affected by such solvents as carbon bisulfide, aniline, nitrobenzene, amyl alcohol,

¹ Brooks and Bacon, *J. Ind. Eng. Chem.*, 6, 623 (1914).

² A. Pictet, *Ber.*, 46, 3342 (1913); Jones and Wheeler, *J. Chem. Soc.*, 105, 2562 (1914); 107, 1318 (1915).

pyridine, ether, acetone, etc., in a manner strictly parallel to the effect of these solvents on the fluorescence of the esters of terephthalic acid studied by Kauffman.¹

(3) Suspensoids of colloidal degree of dispersion were found to be totally absent in strongly fluorescent petroleum oils.

(4) The fluorescent substances are readily sulfonated by strong sulfuric acid, forming water-soluble compounds whose aqueous solutions are strongly fluorescent.

Before considering the matter further it should be recalled that all petroleum products which have been thoroughly examined have been shown to contain benzene and its simpler homologs. Even gasoline distilled from light Pennsylvania crude oil contains small percentages of them. The isolation and identification of the higher benzene homologs has apparently not been attempted, probably owing to the much greater experimental difficulties encountered, although Markownikow² isolated 3,5-diethyltoluene and isoamylbenzene, $C_6H_5.C_5H_{11}$, from the light kerosene distillate of Baku oil and H. O. Jones and H. A. Wootton³ isolated β -dimethylnaphthalene from a Borneo petroleum.

Some Conditions under which Benzene Hydrocarbons are Formed.

It is known that in the manufacture of oil gas at a temperature of about 950° profound decomposition of the oil occurs, with the formation of hydrogen, methane, acetylene, olefines and a series of benzene hydrocarbons. The assumption is probably warranted that whenever the temperature is sufficiently high for the formation of acetylene, aromatic compounds will be found among the reaction products. The lowest temperature at which acetylene can be formed from petroleum oils has apparently not been determined, but no references exist in the literature noting its presence in oil gas made at temperatures lower than 750°. It is known that under certain conditions naphthenes may form benzene hydrocarbons, accompanied by the splitting off of hydrogen, and the work of Nikiforoff and Ogloblin⁴ shows that by employing heat alone temperatures of at least 525–550° are necessary.⁵ Engler⁷ obtained no free hydrogen whatever by heating kerosene to temperatures below 470°. Although cyclohexane and methyl cyclohexane have been con-

¹ *Ann.*, 393, 1 (1912).

² *Ibid.*, 234, 89 (1886).

³ *J. Chem. Soc.*, 91, 1146 (1907); *Chem. Zent.*, 1907, II, 1029.

⁴ W. A. Noyes, *THIS JOURNAL*, 16, 688 (1894).

⁵ *Z. angew. Chem.*, 18, 546 (1905).

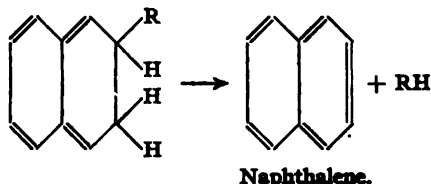
⁶ Since the outbreak of the war in Europe, benzene and toluene have been made from petroleum on a commercial scale in several plants using the Hall process, which method employs a temperature of about 650° and pressures of 50 to 75 pounds per square inch and by the Rittman process employing slightly higher temperatures and pressures.

⁷ "Das Erdöl," Vol. I, p. 574.

verted into benzene and toluene, respectively, by splitting off hydrogen in the presence of metallic catalysts, such as nickel, platinum and palladium at temperatures below 300° , these conditions are widely removed from the conditions of the experiments described in this paper.

We have found that the heavier portion of Jennings and Oklahoma crude petroleum, *i. e.*, that part remaining after removing by distillation those fractions boiling below 275° , and hereinafter designated as reduced oil, yields benzene, toluene and xylene by "cracking" at temperatures not exceeding 420° and under 100 pounds' pressure; that these aromatic hydrocarbons are also obtained by cracking Jennings and Oklahoma reduced oils by heating with anhydrous aluminum chloride; that pure paraffin wax on cracking under either of these conditions does not yield benzene or its homologs, nor does it yield fluorescent distillates; that synthetic phenyl-paraffin, made by condensing chloroparaffin with pure benzene, is readily cracked by heating to 420° under 100 pounds' pressure or by merely heating with aluminum chloride to 230° yielding benzene and toluene among the reaction products. It is noteworthy, too, as agreeing with the above noted theory of the nature of the fluorescent compounds in petroleum, that, while the decomposition products of pure paraffin are not fluorescent, the introduction of a benzene nucleus leads to decomposition products which are highly fluorescent.

Jones and Wheeler¹ have shown that certain aromatic hydrocarbons are produced in the distillation of coal *in vacuo* at 350° and point out that this is below the temperature at which hydrogen is split off. They suggest that a reaction of the following type may take place:



In view of the facts recorded in this paper, we believe that the formation of free naphthalene at 350° , as noted by Jones² and Wheeler, is better accounted for by the decomposition of a complex molecule containing

¹ *J. Chem. Soc.*, 105, 2562 (1914).

² In a recent paper [*J. Chem. Soc.*, 107, 1582 (1915)], Jones states that cyclohexane, methyl cyclohexane and tetrahydronaphthalene began to decompose at approximately the same temperature namely, between 490° and 510° . The gas evolved contained approximately 40% hydrogen. Dihydronaphthalene decomposed at 390° and the gas evolved contained 80% hydrogen. The important bearing of Jones' work upon the matter here presented is the confirmation of the earlier work that a temperature of 500° is necessary to form benzene or toluene from cyclohexane and methyl cyclohexane, respectively, and that this decomposition of cyclohexane occurs relatively much easier than in the case of the normal paraffines.

the naphthalene radical, in the same way as we have shown phenyl-paraffin to be broken down into benzene, toluene and unsaturated hydrocarbons. For example, $C_{10}H_7 \cdot C_nH_{2n+1} \rightarrow C_{10}H_8$ (naphthalene) + C_nH_{2n} (olefine of naphthene).

Experimental Part.

The Oklahoma reduced oil employed in the following experiments had the specific gravity 0.877, $20^\circ/4^\circ$, all material boiling below 275° having been distilled from the mixture. Three liters of the oil were cracked by slowly distilling under 100 pounds' pressure in a small iron still, capacity about 5.5 liters, the temperature gradually rising during the distillation through the range $375\text{--}415^\circ$. After three hours the distillate, 75% of the charge, was redistilled at atmospheric pressure and the fraction boiling below 150° , amounting to 22% of the charge was collected separately.¹ This low boiling portion was extracted at -15° with liquid sulfur dioxide. This extraction was carried out by shaking in a large Dewar flask with an equal volume of liquid SO_2 divided into three portions which were added successively after siphoning off the heavy layer from the preceding treatment. From the sulfur dioxide solution there were recovered about 10% by volume of the gasoline fraction, or 2.2% of the original charge of reduced oil. This was fractionated three times and the fractions boiling at $75\text{--}85^\circ$, $105\text{--}115^\circ$ and $135\text{--}145^\circ$ were nitrated first in the cold and finally on a steam bath with an excess of ordinary sulfuric and nitric acids. The crude crystalline masses obtained by pouring into water were recrystallized and pure 1,3-dinitrobenzene, m. p. 90° , also 2,4-dinitrotoluene, m. p. 70° , and 2,4,6-trinitrometaxylene, m. p. 182° , were isolated.

We then examined the gasoline obtained by heating heavy high boiling oils with anhydrous aluminum chloride. Twenty liters of Oklahoma reduced oil were heated with 6% anhydrous aluminum chloride until four liters of light distillate were collected. When this was extracted with $\frac{1}{2}$ volume liquid sulfur dioxide 0.40 liter extract was obtained. On fractionating and nitrating the proper fractions as before, pure 1,3-dinitrobenzene, 2,4-dinitrotoluene and 2,4,6-trinitro-*m*-xylene were isolated.

In order to determine quantitatively the amounts of aromatic compounds present in cracked gasolines, and in order to compare these results with those given by several natural gasolines distilled from crudes, we extracted a series of gasolines by using a total of 1.5 volumes of liquid sulfur dioxide in three successive extractions at -15° in Dewar flasks. The following tabulated results include a sample of gasoline made by cracking Texas Solar oil with aluminum chloride:

¹ Cf. Brooks, Bacon, Padgett and Humphrey, *J. Ind. Eng. Chem.*, 6, 180 (1914); Brooks, *J. Franklin Inst.*, 1915, p. 653 (December).

TABLE I.—COMPARISON OF NATURAL GASOLINE AND THAT OBTAINED BY CRACKING WITH RESPECT TO AROMATIC COMPOUNDS.

Gasoline source.	Volume of sample treated, cc.	Per cent. soluble in SO ₂ .	Fractionation of SO ₂ . Soluble portion, per cent.			Grams dinitro-toluene.	Grams trinitro-xylylene.
			to 90° C.	90°–120°.	120°–145°.		
Bristow crude.....	1000	4.5	9.0	48.8	17.7	1.6	..
Muskogee crude ¹	1000	13.0	6.1	42.3	23.0	4.1	17.4
Mexican crude.....	1000	14.0	31.4	27.1	17.1	0.9	..
California crude....	750	13.0	20.0	58.0	19.0	4.4	..
Texas solar oil by AlCl ₃	1000	32.5	23.0	26.1	16.9	13.8	39.6

Relative Stability of Paraffins and Naphthenes. -

In cracking commercial paraffin, we were surprised to find that this material is more difficult to decompose than light lubricating oil which is composed almost exclusively of naphthenes and polynaphthenes. While the simpler naphthenes whose constitutions are known, such as cyclohexane and methyl cyclopentane, are apparently more stable to heat than normal paraffins, and have been found among the products resulting from heating simple paraffin hydrocarbons under pressure,² the instability of the three- and four-membered rings in the terpene series is well-established. The properties of cycloheptane, cyclooctane, cyclononane and their derivatives are not so well known, but their tendency to rearrange to five- and six-ring systems has been frequently observed. It is probable that the relatively greater ease of cracking petroleum naphthenes, such as constitute much the greater part of light lubricating oil, as compared with the cracking of commercial paraffin wax of substantially the same average molecular weight and boiling point range, is to be interpreted as indicating that these high boiling naphthenes belong to series other than of five- or six-membered rings. The behavior on heat decomposition of naphthenes of known constitution such as cyclooctane, cyclononane, or their derivatives is not known.

That the heavy residues of certain crudes are more easily cracked than others is known to refiners. Heavy Mexican crude, particularly, is readily decomposed by heat and is conspicuous for its extremely high coke residue. (By slow direct fire distillation we have noted coke residues from this crude as high as 42%.) That higher temperatures are required for the cracking of paraffin than for reduced Jennings oil, made up of naphthenes and polynaphthenes and free from paraffin and from which all constituents boiling below 275° had been removed, was shown in two parallel distillations made under 100 pounds' pressure, the temperature being taken about

¹ That the extraction of aromatic hydrocarbons by the SO₂ method, as carried out above, was incomplete was shown by the isolation of 5 grams of dinitrotoluene after nitrating the 100–120° fraction of the portion insoluble in the sulfur dioxide.

² Engler.

ten minutes after distillation had commenced and afterwards at intervals of one hour.

TABLE II.—DISTILLATION OF PARAFFIN AND JENNINGS REDUCED OIL UNDER PRESSURE.

Material distilled.	Time required for distillation. Hours.	Temperature at 1-hour intervals.	Per cent. of charge distilled at last temperature reading.	Product distilling below 150°—per centage of original charge.	Volume of gas evolved per liter oil.
Jennings reduced oil....	3.5	370-415-422°	69.0	19.0	31.36
Paraffin.....	3.5	417-432-437°	71.0	20.5	9.33 liters

The following summarized results show that when anhydrous aluminum chloride is used, commercial paraffin wax decomposes much less readily than the other hydrocarbons studied.

TABLE III.—DECOMPOSITION OF PARAFFIN AND NAPHTHENES WITH ALUMINUM CHLORIDE.

Material treated.	Temperature when first drop distilled and at 1-hour intervals.				Time heated. Hours.	Yield of product, %. Btg. to -150°.	% Al_2Cl_6 .
Jennings reduced oil.....	200°	226°	244°	255°	4.5	22.2	7.0
Texas solar oil.....	175°	190°	194°	210°	4.5	24.5	7.0
Paraffin.....	205°	235°	276°	282°	4.5	4.5	7.0
Phenyl paraffin.....	185°	220°	255°	265°	4.5	15.0	7.0

The Cracking of Synthetic Phenyl Paraffin.

A mixture of phenyl paraffins was made by condensing pure benzene with chlorinated paraffin in the presence of anhydrous aluminum chloride at moderate temperatures, not exceeding 90°. In making up this material the commercial paraffin wax, m. p. 53°, was considered as a mixture of hydrocarbons of the mean molecular formula $C_{24}H_{50}$. Two kilos of melted paraffin were chlorinated until the gain in weight was 251 g., theoretical for $C_{24}H_{49}Cl$, being 201 g. This was treated with 2 liters of pure benzene, a large excess, and 0.5 liter of carbon bisulfide. Anhydrous aluminum chloride was then added in small portions until 150 g. had been added. The evolution of hydrogen chloride was very rapid at first, but after standing at room temperature for 14 hours had nearly ceased. The reaction mixture was then gently warmed for six hours on a steam bath, after which time it was washed several times with hot water to remove aluminum chloride and then distilled with steam until liquid ceased to distil, the CS_2 and excess benzene being thus completely removed. After separating from water, the product was heated several hours in a large porcelain dish until all emulsified water had been driven off and then finally heated to 250° to insure the complete removal of free benzene. The dried material was then divided into two portions, one portion of 500 g. being heated with 35 g. anhydrous Al_2Cl_6 to temperatures within the range 200-240°, the distillate being partially refluxed through a fractionating column. In

3 hours 78 cc. of distillate were collected. This was redistilled and 55 cc. of benzene, b. p. 79–85°, and 11 cc. toluene, b. p. 105–115° were obtained.

The identity of the benzene and toluene was further proved by conversion into the corresponding dinitro derivatives. The dinitrobenzene obtained, after recrystallizing, melted at 90° and the dinitrotoluene at 70°. Since pure benzene of tested purity and free from toluene was employed for the synthesis, the presence of toluene can be accounted for only by the splitting of the phenyl paraffin, $C_6H_5CH_2 \mid CH_2R$. In this reaction the higher boiling portion of the material was converted into a mixture of naphthenes. After pouring off the warm residue from the aluminum chloride and pitch, the oil was chilled and about 32 g. of crystalline paraffin were filtered from it. The filtered oil was then a viscous material resembling light lubricating oil but possessing an *intense green fluorescence*, resembling very closely the highly fluorescent oil obtained by treating Mexican crude petroleum with a small amount of aluminum chloride.

Two and one-half kilos of phenyl paraffin, prepared as above, were subjected to distillation under 75 pounds' pressure for three hours. The 1510 cc. of distillate were redistilled giving the following:

TABLE IV.—RESULTS OF DISTILLING PHENYL PARAFFIN UNDER 75 POUNDS' PRESSURE.

Fraction of product.	Quantity, cc.	Result on nitration
70–100°	112	25 g. crude dinitrobenzene
100–115°	150	41 g. crude dinitrotoluene
115–145°	272	

The isolation of dinitrotoluene, melting point of recrystallized product 69.2°, from the products of the distillation of phenyl paraffin under pressure shows, as in the case of decomposition by aluminum chloride, that the phenyl paraffin can break down so as to give not only benzene but toluene and possibly other homologs.

As regards the character of the fluorescent hydrocarbons in petroleum it was noted that the residue from the distillation of pure paraffin was not fluorescent, although if the distillation had been carried further so as to form considerable coke, the oil residue would undoubtedly have been fluorescent.

Summary.

(1) Benzene and toluene and *m*-xylene have been found among the products from the cracking of heavy petroleum oils by (a) distillation at temperatures not exceeding 420° and pressures not exceeding 100 pounds, and (b) heating with anhydrous aluminum chloride to temperatures not exceeding 300°.

(2) Commercial paraffin wax does not yield benzene, toluene or xylene under the conditions just named.

(3) Synthetic phenyl paraffin, made from pure benzene and chlorinated paraffin, yields benzene and toluene among the reaction products under the conditions named in (1).

(4) From the above facts the conclusion is drawn that the heavy high boiling fractions of petroleum contain homologs of benzene, or hydrocarbons containing the benzene nucleus.

(5) The high boiling residues from the decomposition of phenyl paraffin are highly fluorescent, which supports the theory advanced in an earlier paper that the fluorescence of petroleum oils is due to the presence of complex hydrocarbons related to benzene.

PITTSBURGH, PA.

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF ILLINOIS.]

THE STRUCTURE OF THE DIHYDRO- β -NAPHTHOIC ACIDS.

By C. G. DERICK AND OLIVER KAMM.¹

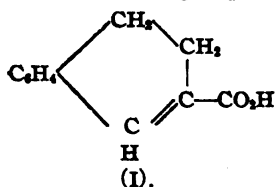
Received December 18, 1915.

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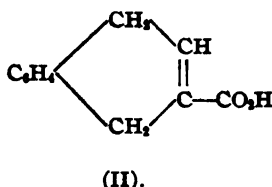
I. Introduction. II. The Third Isomeric Dihydro- β -naphthoic Acid. III. Proof of the Atomic Linking Structures of the Three Dihydro- β -naphthoic Acids from the Chemical Behavior of Their Respective Dibromides. IV. Proof of the Atomic Linking Structure of the Third Dihydro- β -naphthoic Acid by Oxidation. V. A Correlation of Structure and Odor. VI. Experimental Part.

I. Introduction.

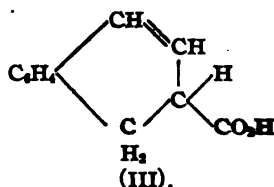
Three dihydro- β -naphthoic acids which have an unsaturated linkage in the ring carrying the carboxyl group are theoretically possible, their structures being represented as follows:



Δ^1 -Dihydronaphthoic acid-2.²



Δ^2 -Dihydronaphthoic acid-2.



Δ^1 -Dihydronaphthoic acid-2.

Of the above acids, two have previously been prepared and the structure of one of them has been definitely demonstrated. In the present work, which was carried out in connection with a study of the correlation of ionization and structure, the third isomeric acid has been prepared and demonstrations of the structures of the three isomers have been developed.

By the reduction of β -naphthoic acid with sodium amalgam, Sowinski³ obtained two of the isomeric acids represented above. This work is also

¹ Presented at the Cincinnati meeting (1914) of the American Chemical Society. From a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Illinois (Kamm, 1915).

² The nomenclature used is that given in Meyer and Jacobson's "Lehrbuch der Organischen Chemie," 1903, Vol. 2, Pt. 2, p. 446.

³ *Ber.*, 24, 2354-2363 (1891).

reported by Baeyer and Besemfelder,¹ who obtained the acids in a higher state of purity. By reduction with sodium amalgam in the cold a mixture consisting chiefly of the labile acid (so-called because of the ease of its rearrangement into the higher-melting stable isomer) was obtained, while reduction in hot solution yielded chiefly the stable acid. The mixture obtained in either case was separated, due to the different solubilities of the two isomers in water.

Structure III (above) has been assigned by Baeyer and Besemfelder to the labile acid not only because of the ease of its rearrangement into the stable isomer but also because they found that with bromine it formed an unstable dibromide which decomposed spontaneously into a monobromolactone. This indicates that a bromine atom was initially present in the gamma position with respect to the carboxyl group which is possible only in the case of the dibromide derived from Structure III. The same acid, because of the asymmetry of its molecule, should be capable of existing in two optically active components, and that such is the case has been shown by Pickard and Yates² who have prepared *d*- Δ^2 -dihydronaphthoic acid-2. This is a further confirmation of the structure of the labile acid since the two other isomers represent symmetrical structures.

The stable dihydro acid obtained by rearrangement of the labile acid must therefore possess one of the two remaining structures (I or II above). Baeyer,³ as well as Meyer and Jacobson,⁴ from the data at hand have not attempted to differentiate between the two possible structures. Formula II has been suggested by Besemfelder⁵ as the most probable structure because of the ease with which β -naphthoic acid is formed when the corresponding dibromide is digested with alcoholic potash. Under similar conditions, however, the monobromolactone derived from the labile dihydro acid also yielded β -naphthoic acid. It is therefore evident that the behavior of its dibromide with alkali is an unsafe criterion for the assignment of the structure of the stable acid unless the dibromides of both the Δ^1 and Δ^2 dihydro acids have been treated in this manner. This is now possible, for in the present work the third isomeric dihydro acid has been prepared. The dibromide of Baeyer's labile dihydro acid has also been prepared and found to be fairly stable, not undergoing spontaneous decomposition as reported. It is therefore possible to study side by side the reactions of the dibromides of the three isomers. The structure of the new dihydro acid has, however, been demonstrated independently by means of its oxidation products.

¹ *Ann.*, 266, 187-202 (1891).

² *J. Chem. Soc.*, 95, 1011-1015 (1909); *Chem. Zentr.*, [2] 1909, p. 445.

³ *Ann.*, 266, 174 (1891).

⁴ *Loc. cit.*

⁵ *Ann.*, 266, 198 (1891).

II. The Third Isomeric Dihydro- β -naphthoic Acid.

When the stable dihydro acid (m. p. 161°) is treated with water and an excess of barium hydroxide in a sealed tube at a temperature of 160 – 180° , the third isomeric acid is formed. Its melting point after purification is found to be 118.5° (cor.). The same product may be obtained from the labile isomer, although in some cases it is found contaminated with the 161° stable acid, indicating that the rearrangement has taken place with the formation of the latter as an intermediate product.

We might suggest Structure I as that of the new acid on the basis of this rearrangement, since we would expect the acid having the unsaturated union in intimate relation to both the carboxyl group and to the phenyl ring to be the most stable toward rearrangement. This has already been stated by Baeyer, who has suggested the possibility of preparing the third isomer by a method analogous to the one used.

The method of preparation of the 118° acid (Δ^1) suggests that the same object might be accomplished by means of a strenuous treatment with concentrated potassium hydroxide solution at ordinary pressures and such was actually found to be the case. When either the labile or the Δ^2 stable acid is boiled with a solution of potassium hydroxide (1 : 2) for about eight hours, a 75% yield of the third isomer is obtained. It is separated from any unchanged acid and from the small amount of β -naphthoic acid formed by oxidation by means of fractional precipitation. It is obtained in a higher state of purity from its dibromide.

The 118° acid is analogous to the other stable acid (Δ^2) and to Δ^1 unsaturated acids in general in its behavior. It is attacked instantaneously by potassium permanganate and with an excess is destroyed. In the cold it adds bromine slowly. It was characterized by means of its dibromide and its amide as well as by analysis and a determination of its neutral equivalent. Additional tests of its homogeneity as a pure chemical individual are discussed in the experimental part of this paper.

III. Proof of the Atomic Linkage Structures of the Three Dihydro- β -naphthoic Acids from the Chemical Behavior of Their Respective Dibromides.

As already mentioned, Baeyer and Besemfelder were able to prepare the dibromide of only one dihydro acid, the dibromide of the labile acid undergoing spontaneous decomposition with the evolution of hydrobromic acid. By using a somewhat different procedure the dibromides of all three isomers may be prepared without meeting any of the difficulties encountered by previous investigators. The dihydronaphthoic acids are all very soluble in chloroform while their dibromo derivatives are not. The method used was to dissolve the acid in chloroform and to add the calculated amount of bromine also dissolved in chloroform,

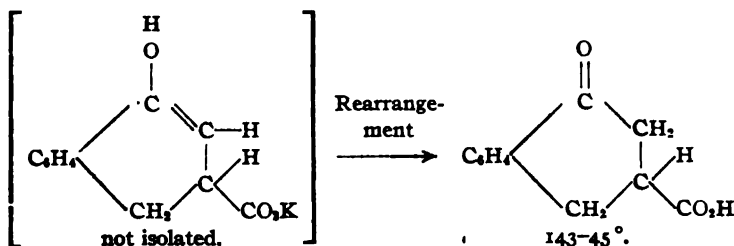
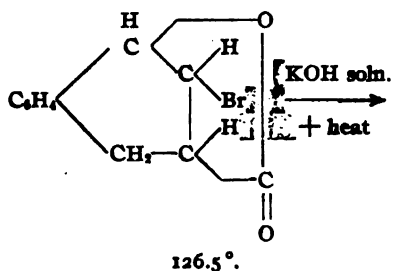
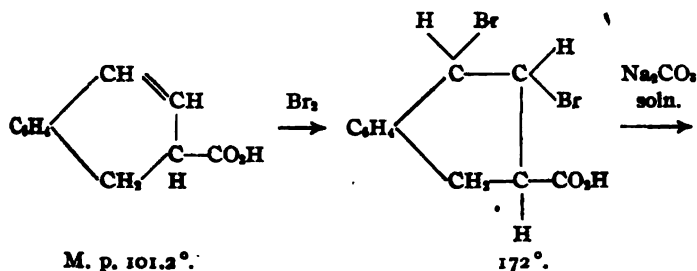
keeping the mixture cold. Under these conditions the dibromo derivatives separate out in the form of white crystals.

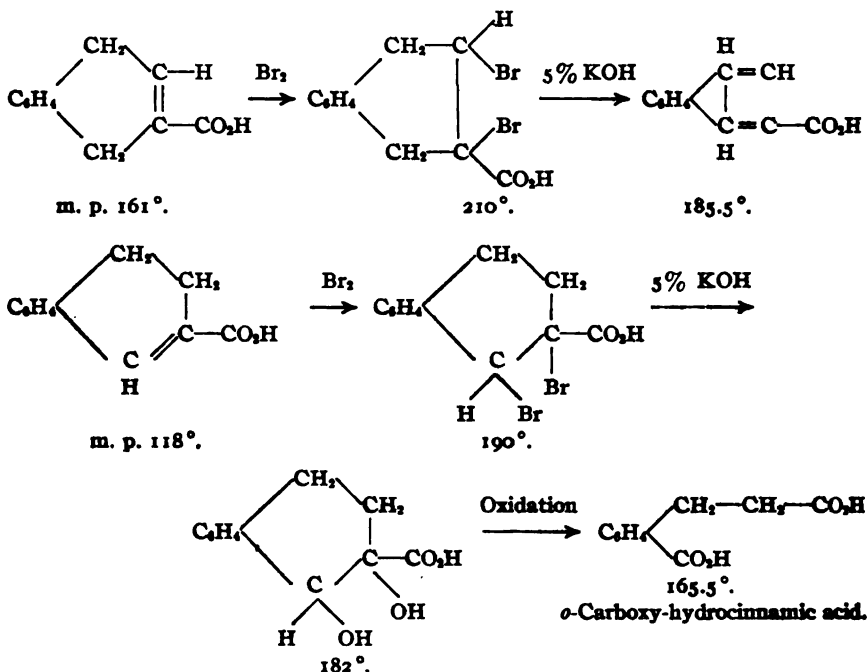
The melting points of the acids and of the corresponding dibromides are as follows:

TABLE I.

	M. p.	M. p. of dibromide.
Labile Δ^2 acid.....	101.2°	172° with decomp.
Stable Δ^1 acid.....	118°	190° with decomp.
Stable Δ^3 acid.....	161°	210° with decomp.

Behavior of the Dibromides with Alkalis.—The three dibromides react in so characteristic a manner with dilute alkalis that this behavior may be used as a demonstration of the structure of the dibromides themselves and therefore of the corresponding unsaturated acids. In these decompositions it is unnecessary to use boiling alcoholic potash, in fact the best results are usually obtained with a cold 10% aqueous solution of sodium carbonate. The reactions observed are as follows:





The dibromide of the labile dihydro acid (Δ^4) when treated with sodium carbonate solution at first dissolves completely. Soon, however, a turbidity is observed and after a few minutes the monobromolactone separates. The dibromide of the stable (Δ^2) isomer dissolves readily in dilute alkali to a clear solution, although it is decomposed rapidly and almost quantitatively into β -naphthoic acid. This decomposition takes place even at a temperature of 0° (although more slowly), no color changes being apparent. The dibromide of the 118° acid (Δ^1), on the other hand, undergoes the characteristic reactions observed when an α,β -dibromo acid is treated with alkali. If the solution is warmed, a deep blue color develops slowly, but finally disappears, a yellow solution remaining. At the same time a trace of an indifferent substance separates, due probably to the decomposition of an unstable β -lactone.¹ No trace of β -naphthoic acid is formed, the main product being the dihydroxy acid represented above. Its formation is analogous to the decomposition of α,β -dibromohexahydrobenzoic acid observed by Aschan.² Independent evidence of the structure of this dihydroxy derivative and therefore of the Δ^1 -dihydro acid itself is offered by the oxidation of the dihydroxy acid to *o*-carboxy-hydrocinnamic acid of known structure.

¹ The reactions of dibromocinnamic acid may be taken as an example. Nef *Ann.*, 308, 267 (1899); Fittig-Kast, *Ann.*, 206, 33 (1881).

² *Ann.*, 271, 281 (1893).

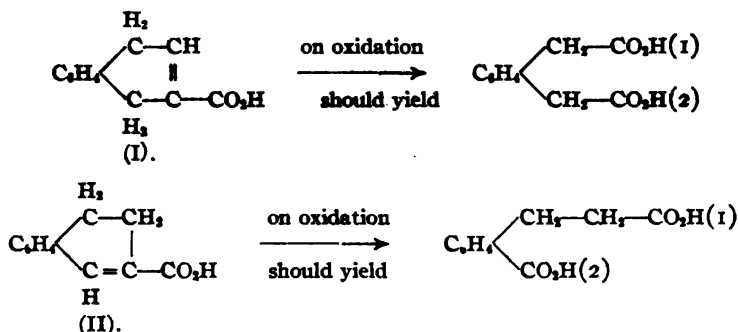
The reactions of the dibromides outlined above demonstrate that the three dihydro acids described are distinct chemical individuals. The results confirm the conclusions of Baeyer and Besemfelder in regard to the structure of the labile dihydronaphthoic acid (Structure III). Moreover, since the structure of this acid is known, and since we have prepared the third isomeric acid and its dibromide and made a study of the decomposition products of the latter, we may now accept the reactions of the dibromide of the stable (161°) acid as conclusive evidence that Structure II is correct, while Structure I should be given to the new isomer (118° acid). Independent evidence in regard to the structure of the latter is, however, presented below.

More recently it has been found¹ that the dibromides of the dihydro- α -naphthoic acids react in an exactly analogous manner to that observed in the β -naphthoic acid series. This evidence can be used on the one hand to demonstrate the structures of the corresponding dihydro- α -naphthoic acids, and on the other is additional evidence in favor of the use of the reactions of these dibromides for the demonstration of structure.

IV. Proof of the Atomic Linking Structure of the Third Dihydro- β -naphthoic Acid by Oxidation.

Although the reactions of the dibromides present satisfactory evidence in favor of the structures of the corresponding dihydro acids, it was considered advisable to demonstrate the structure of the new isomer in an entirely independent manner. The method chosen was that of oxidation.

Meyer and Jacobson² state that the stable acid of Baeyer has either Structure I or Structure II below.



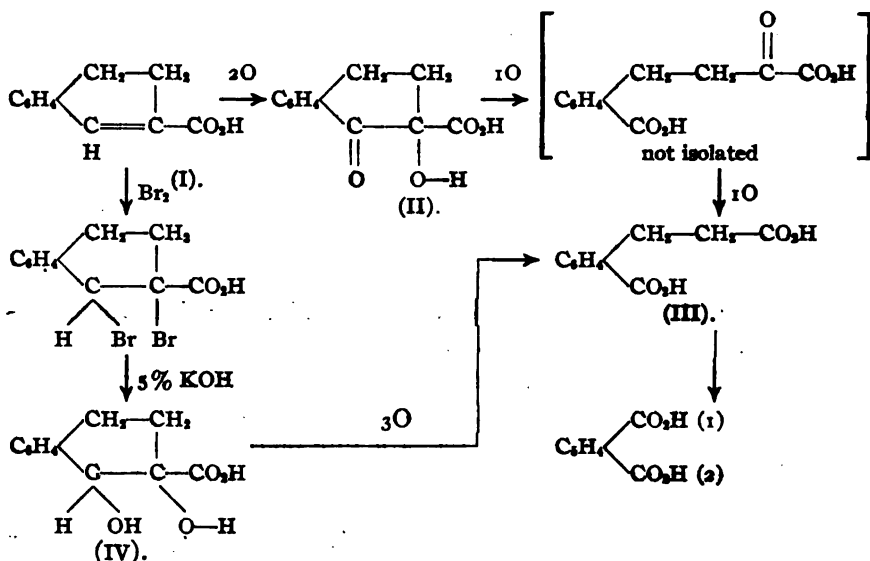
For this demonstration of structure by means of oxidation reactions, the new isomeric acid Δ^1 -dihydronaphthoic acid-2 was used, the oxidizing agent being alkaline potassium permanganate. Using this method,

¹ Kamm and McClugage. See the following article in THIS JOURNAL.

² *Loc. cit.*

Baeyer and Shroder¹ had succeeded in demonstrating the structure of Δ^1 -dihydronaphthoic acid-1, since upon oxidation *o*-carboxyhydrocinnamic acid was obtained. The β -isomer under examination should yield the same final product, and such was found to be the case. It was necessary, however, to apply very radical changes to the Baeyer method, since the first attempts always yielded products contaminated with large amounts of phthalic acid. The modified method adopted was to carry on the oxidation in steps, using the theoretical amounts of permanganate.

The reactions observed were as follows:



The keto-hydroxy acid (II) was obtained in 50-60% yield, and from it pure *o*-carboxyhydrocinnamic acid (III) was obtained in 40% yield. The latter product was also obtained from the dihydroxy acid (IV).

The structures of the three theoretically possible dihydro- β -naphthoic acids have thus been definitely established by analytical methods, and a study of the correlation of ionization and structure in this series may now be made.

V. A Correlation of Structure and Odor.

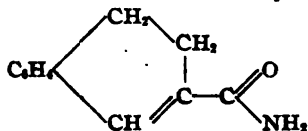
An interesting correlation between chemical structure and odor was noticed during the course of this study. When the amides of the various naphthoic acids, discussed in this paper, were prepared, it was noted that of the three dihydro- β -naphthoic acids, only the two stable isomers gave amides which possessed a very marked cinnamon-like odor. This was especially noticed in the case of the new isomer, Δ^1 -dihydronaphthoic acid-2. Accordingly, the amide of cinnamic acid was prepared and was

¹ *Ann.*, 266, 176 (1891).

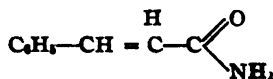
found to possess an identical odor. This cinnamon-like odor is known to be characteristic of the side-chain linkage $>C = C - C -$, as was



learned from cinnamic aldehyde. The analogy in structure is apparent.



Amide of Δ^1 -dihydronaphthoic acid-2.



Amide of cinnamic acid.

The melting points of the amides prepared in this work are given in Table II. The amide of cinnamic acid is included since the literature gave the widely varying values 141.5° and 147° .

TABLE II.

Acid.	M. p.	M. p. of amide.	Acid.	M. p.	M. p. of amide.
Beta-naphthoic.....	185°	195°	Stable dihydro-naphthoic..	118°	155°
Tetrahydro-naphthoic....	96°	137°	Stable dihydro-naphthoic..	161°	168°
Labile dihydro-naphthoic.	101.2°	$140-50^\circ$	Cinnamic.....	133°	148°

VI. Experimental Part.

The Preparation of β -Naphthoic Acid.—This acid was prepared using the Sandmeyer reaction,¹ starting with a pure grade of β -naphthyl amine. The nitrile was distilled with steam and hydrolyzed as outlined below. This method yielded an exceptionally pure grade of β -naphthoic acid, which after one crystallization from dilute acetic acid melted at 185° . The yield was, however, less than 20% of the theoretical. For the preparation of large amounts of the acid, the following method was found to be more satisfactory: β -Naphthalene sulfonic acid was prepared in the usual manner by treating naphthalene with concentrated sulfuric acid at 180° . The β -sulfonic acid was separated as the calcium salt,² recrystallized from water and then converted into the sodium salt. The yield of the latter was 625 grams from one kilo of naphthalene. A more convenient, more rapid, and more efficient method for preparing the pure β -sulfonic acid has recently been published by Witt.³ Naphthalene is sulfonated by heating it for a few minutes at 160° . The clear homogeneous liquid is poured into water, small amounts of sulfone and unchanged naphthalene separated, and the acid solution evaporated to a smaller bulk. The β -isomer crystallizes out as the tri-hydrate and is obtained pure after a recrystallization from 10% hydrochloric acid. The separation of the two isomeric sulfonic acids through their calcium salts is therefore unnecessary.

¹ Gattermann, "Practical Methods of Organic Chemistry," eleventh edition (translated, 1914), p. 248.

² Ber., 3, 196 and 710; Gattermann, *Loc. cit.*, p. 291.

³ Ber., 48, 751-753 (1915).

The nitrile was prepared in the usual manner by subjecting to dry distillation the sodium salt intimately mixed with an equal weight of potassium ferrocyanide. The yield of crude nitrile was 120 g. from 625 g. of sodium sulfonate, but can be improved by conducting the dry distillation under diminished pressure, or by distilling the mixture in small quantities. The yield of naphthoic acid from hydrolysis of 120 g. of nitrile was 100 g. The method was materially improved in the following manner: In the dry distillation with potassium ferrocyanide, the yield is exceptionally poor if the calcium sulfonate is fused directly. If, however, potassium cyanide is used, the calcium salt itself may be substituted, without converting it into the more fusible sodium salt. 40 g. of calcium sulfonate mixed with an equal weight of potassium cyanide and distilled in four portions yielded 18 g. of crude nitrile from which an almost equal weight of crude naphthoic acid was obtained.

The nitrile was hydrolyzed as directed by Baeyer and Besemfelder,¹ using a mixture of equal volumes of concentrated sulfuric acid, glacial acetic acid and water. The material, which Baeyer and Besemfelder report as insoluble in sodium carbonates solution should, however, not be discarded as directed but should be boiled with 20% KOH solution, thus increasing the yield of the acid. This insoluble material consists largely of the amide. A sample of the nitrile which had been purified by distillation was found to saponify more smoothly. It was in this case easily possible to stop the hydrolysis at the amide stage. The crude β -naphthoic acid was precipitated as the barium salt from a dilute hot solution of its sodium salt by means of barium chloride solution. The free acid was recovered by recrystallization from 30 to 50% acetic acid, treated with bone-black, and purified by fractional crystallization. The pure acid melted² at 185.5°. Its amide (m. p. 195°) was prepared using one mol of phosphorus pentachloride and decomposing the acyl halide with ammonia water. It was also obtained (m. p. 194°) in the hydrolysis of the nitrile as mentioned above.

The Reduction of β -Naphthoic Acid.—The reduction with 3% sodium amalgam in the cold, a stream of CO₂ being passed into the solution to neutralize the free alkali, yielded a mixture consisting of 75% labile dihydro and about 25% stable Δ^2 dihydro acids. Reduction in hot solution yielded the same two acids except in different proportions, 40% and 60%, respectively. The labile isomer obtained by reduction in hot solution, however, contains appreciable amounts of the tetrahydro acid, from which it is separated only with difficulty. The methods of reduc-

¹ *Ann.*, 266, 187 (1891).

² The melting points given in this paper refer to the capillary melting points, corrected for stem exposure. The corrections were almost negligible since calibrated Anschütz thermometers were used.

tion and the use of fractional precipitation as described by Baeyer and Besemfelder have been found satisfactory. The advantages of the method of fractional precipitation over that of fractional crystallization for the separation of mixtures of these isomeric acids should be further emphasized. The most soluble isomer is usually also the one having the largest ionization constant, and consequently the separation is unusually effective. The use of too concentrated solutions should, however, be avoided since this will result in the occlusion of the salt by the precipitated acid. The melting points of the acids have either been found to be as reported by Baeyer or slightly higher. Only in the case of the labile isomer was a lower value observed than that reported previously. Since the acid was to be used for conductivity measurements, it became necessary to investigate this point carefully. The melting point found was 101.2° , whereas the reported value is 104° .

Preparation of the Labile Dihydro- β -naphthoic Acid and the Separation of Isomers by Means of Fractional Precipitation.—A typical reduction will be described here. Ten grams of pure β -naphthoic acid were dissolved in a small amount of dilute potassium hydroxide solution and the solution diluted to 100 cc. The latter was then cooled to 5° , a steady stream of carbon dioxide passed into it and 150 g. of crushed 3% sodium amalgam added at one time. Small portions (0.5 cc.) of the solution were withdrawn at ten-minute intervals and tested with potassium permanganate.¹ The reduction was complete in forty minutes. The sodium carbonate solution was separated from the mercury, a few pieces of ice added, and the free dihydro acids precipitated with hydrochloric acid. The precipitate, which consists of white crystals, was dissolved in very dilute potassium hydroxide solution (100–150 cc.) and the dihydro acids precipitated in fractions, using approximately normal hydrochloric acid, adding the latter slowly from a pipet. The ten fractions obtained were almost equal in weight (approximately 1 g. each); the first three consisted of cream-colored flakes, while the others were more granular (typical of the labile isomer) and were pure white.

No. of fraction.	M. p. before recrystallization.		No. of frac.	M. p. before recrystallization.	
1	$155-57^\circ$	} Stable dihydro acid	6	101°	} Recrystallized from 30% acetic acid, m. p. 101.0° Labile isomer
2	$154-56^\circ$		7	100°	
3	$152-54^\circ$		8	100.5°	
4	103.5°	} Mixture of labile and stable acids	9	100.5°	
5	101.5°		10	100°	

¹ The dihydro acids are oxidized under these conditions while β -naphthoic acid is not. The permanganate is added until a permanent color is obtained, a small amount of sodium sulfite then added and the solution acidified. If the reduction is incomplete the sparingly soluble naphthoic acid will precipitate.

Fractions 7 and 8, after recrystallization, were again subjected to fractional precipitation and shown to be homogeneous.

REFRACTIONATION OF FRACTIONS 7 AND 8.

No.	M. p.	No.	M. p.
1a.....	100.2°	4a.....	100.8°
2a.....	100.8°	5a.....	100.6°
3a.....	100.8°	6a.....	100.6°

Fraction 3a was recrystallized from dilute acetic acid. The product consisted of pure white needles melting at 101.1°.

REFRACTIONATION OF FRACTION 4 (M. P. 103.5°).

No.	M. p.		No.	M. p.	
1b	155-56°	} Stable isomer	5b	101°	} Labile isomer
2b	154-56°		6b	101°	
3b	140-50°	} Mixture	7b	101°	
4b	102-3°		8b	100.8°	

Refractionation of Fractions 7 and 8 shows that they are not further purified by a second fractional precipitation. Fraction 4 falls intermediate between the fractions of the stable isomer (m. p. 161°) and the lower melting labile isomer. The results of the refractionation of this one gram fraction illustrates the effectiveness of the method. Fraction 9 was completely destroyed with an excess of potassium permanganate in alkaline solution and an examination of this solution failed to show the presence of tetrahydronaphthoic acid.

Several grams of the dihydro acid (101°) were then converted into the dibromide by the method outlined below. From the pure dibromide, the original dihydro acid was recovered by the action of zinc dust in acetic acid solution. The recovered acid was crystallized from dilute acetic acid and melted at 101°. It was again subjected to fractional precipitation and again shown to be homogeneous. The maximum melting point was 101.2° and was not changed when the acid was recrystallized from low-boiling ligroin.

Rearrangement of the Dihydro- β -naphthoic Acids.

Rearrangement with Barium Hydroxide at 160°.—Two grams of the labile acid (Δ^2 -dihydronaphthoic acid-2) were heated with an excess of barium hydroxide (10 g. + 40 cc. water) in a sealed tube at a temperature of 160° for about six hours. When the tube was opened, a distinct naphthalene-like odor was noticed, although decomposition with the loss of carbon dioxide was only slight. The barium salt of an acid was isolated. It was recrystallized from water and the free acid recovered. The latter melted at 118° and appeared to be a pure compound since its melting point was unchanged on subsequent purification from various solvents.

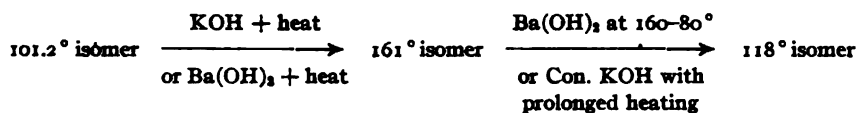
0.1470 g. required 11.00 cc. 0.0764 *N* KOH. Neut. equiv. = 175. Theory for a dihydro acid = 174.

The results are different from those obtained by Baeyer,¹ who prepared a stable isomer melting at 160° by boiling the labile acid in potassium hydroxide solution under atmospheric pressure.

The first experiment was then repeated, the acid being purified not by recrystallization of its barium salt but by means of fractional precipitation. It was found to be homogeneous since each fraction melted within the range of 115 – 117° and all fractions melted at 118° after additional purification.

In a later experiment, however, Baeyer's stable acid (m. p. 161°) was obtained in addition to the 118° product. It was found to be less soluble in water than the latter, and hence the two acids could be partly separated by means of fractional precipitation. The 161° acid is, however, obtained best by the direct reduction of β -naphthoic acid in hot solution, when it is obtained together with the labile isomer from which it may be separated more readily.

The stable acid (161° , now known to be Δ^2 -dihydronaphthoic acid-2) was also treated with barium hydroxide under high pressure as had been the case with the labile isomer. Here also the new acid (m. p. 118°) was obtained in addition to some unchanged product. The following diagram will represent the changes involved:



Both experiments were repeated using potassium hydroxide solution in place of barium hydroxide. The results were identical with those reported above. Variations in temperature and in the time of heating have also been used, but the results are similar to those given above and details will not be repeated here.

Rearrangement under Atmospheric Pressure.—The rearrangement of the labile and stable acids using potassium hydroxide solution at atmospheric pressure was also investigated. Three grams of the labile isomer (m. p. 101°) were boiled under a reflux condenser with 10% potassium hydroxide solution for about one hour. The mixture of acids obtained was separated by fractional precipitation and found to consist of almost equal quantities of the stable isomer (161°) and unchanged labile acid. The 118° isomer was not observed. This confirms the results reported by Baeyer and Besemfelder. It should be noted, however, that the amount of β -naphthoic acid formed during this rearrangement, due to the oxidation of the stable isomer by the oxygen of the air is almost negligible. Baeyer's statement² that the rearrangement is not a

¹ *Ann.*, 266, 192 (1891).

² *Loc. cit.*, p. 192.

smooth one may be explained better by the following experiments: Thirteen grams of the labile isomer (m. p. 101°) which had been prepared and purified as described above were heated for four hours in a more concentrated potassium hydroxide solution than had been used in the previous experiment. (50 g. KOH dissolved in 100 cc. H_2O). Fractional precipitation yielded the fractions indicated below. It will be noted that the first four fractions consist chiefly of the stable isomer (161°) but appear to be less pure than the corresponding acid prepared by heating the labile isomer with more dilute potassium hydroxide solution. These low melting points are not due to admixture with β -naphthoic acid as Baeyer supposed, but are accounted for by the presence of the 118° isomer which is only slightly more soluble than the 161° isomer. Fractions 6 and 7 give evidences of the presence of the new isomer (118°) while the remaining fractions consist of unchanged labile acid. Fractions 1 to 7 were combined and again boiled with 1 : 2 KOH for four hours. In the same manner, Fractions 8 to 13 were combined and boiled with 1 : 2 KOH for eight hours. The second column of melting points represents the fractions obtained after the second treatment with concentrated potassium hydroxide, while the last column gives the melting points of the fractions after recrystallization from acetic acid.

No.	M. p.	No.	M. p.	Recrystallized from 30% acetic acid.
1.....	$145-50^{\circ}$	1a	$114-15^{\circ}$..
2.....	$145-50^{\circ}$	2a	$114-15^{\circ}$	115.5°
3.....	$145-47^{\circ}$	3a	114°	115.5°
4.....	$140-45^{\circ}$	4a	114°	114.5°
5.....	$124-27^{\circ}$	5a	114°	114.5°
6.....	117°	6a	101°	..
7.....	116°
8.....	100°	1b	$113-14^{\circ}$..
9.....	99°	2b	$113-14^{\circ}$	115.5°
10.....	99°	3b	$113-14^{\circ}$	115°
11.....	100°	4b	$113-14^{\circ}$	115°
12.....	100°	5b	112°	115°
13.....	99°	6b	$107-10^{\circ}$	112°
...	...	7b	$95-100^{\circ}$	110°

Fractions 2b to 5b were converted into the barium salt, the latter was recrystallized and the free acids recovered (m. p. 116°).

These results show that both the labile and the stable isomers may be rearranged almost completely into the new isomeric acid (m. p. 118°), the rearrangement of the labile isomer proceeding through the intermediate so-called stable isomer (161°). It is apparent also that the new isomer is contaminated with a less soluble impurity from which it is not completely separated by means of fractional precipitation or by recrystallization.

Comparative conductivity measurements on the 116° sample obtained above and the purer 118° acid obtained by the barium hydroxide treatment, showed no difference in conductivity between the two samples. The impurity present in the 116° sample must therefore be the stable isomer (161°) which is less soluble, or extremely small amounts of the more highly ionized β -naphthoic acid. This problem was investigated quantitatively and it was found that the impurity corresponded to only 2% of the total weight of the 116° sample.

Purification of the 118° Isomer through the Dibromide.—Five grams of the 115 – 16° sample were converted into the dibromide, using the method outlined below. From the dibromide, the dihydro acid was recovered and found to melt at 118° . This recovered product was subjected to fractional precipitation and shown to be homogeneous. The maximum melting point of the 118° acid after recrystallization from ligroin was 118.5° . The chloroform mother liquors from the precipitation of the dibromide were allowed to evaporate spontaneously to one-half volume and a second smaller group of dibromide recovered. The chloroform filtrate was extracted with dilute alkali to remove the last traces of the dibromides as well as any unchanged dihydro acids together with naphthoic acid. From this alkaline extract, 0.10 g. of β -naphthoic acid was recovered. This might have been present in the 116° sample as such or it may have been formed from the action of alkali upon small amounts of the dibromide of the stable (161°) isomer. This separation of traces of 161° acid from the 118° isomer was repeated with known mixtures, and found satisfactory. These reactions are described in detail below, in addition to other tests showing the 118° acid to be a pure chemical individual and not a eutectic mixture.

Δ^1 -Dihydronaphthoic Acid-2 (118° Isomer).—The structure of this isomer is demonstrated below. A brief description of the acid together with some additional tests which have shown it to be a distinct chemical individual will be given here.

Analysis of 118° acid:

Subst. 0.1798; CO_2 , 0.4982; H_2O , 0.0923. Calc. for $\text{C}_{11}\text{H}_{10}\text{O}_2$: C, 75.8; H, 5.79. Found: C, 75.6; H, 5.75.

The analysis, the determination of the neutral equivalent given above, and the fact that the acid forms a dibromide, together with the analysis of the latter (below) proves that we are dealing with a dihydronaphthoic acid. To this we may add that the original acid, unchanged in melting point, is recovered from its dibromide as well as from its amide after purification of these derivatives. This would not be the case if we were dealing with a mixture. The 118° isomer is oxidized instantaneously by potassium permanganate in alkaline solution as is the case with other unsaturated acids. Five grams of the pure acid were dissolved in very

dilute potassium hydroxide solution adding just enough alkali to dissolve the acid completely. The acid was then oxidized in the cold by the addition of 10 g. of potassium permanganate dissolved in 300 cc. water, the oxidizing agent being added slowly in the cold. After filtering off the MnO_2 , the solution was evaporated on the water bath to a smaller bulk (50–100 cc.). Upon acidification of the clear, light yellow solution with mineral acid, no precipitate was obtained, showing the absence of both naphthoic acid and tetrahydronaphthoic acid. From the acidified solution some phthalic acid was obtained by ether extraction.

When a solution of several grams of the new isomer in chloroform was treated with bromine in chloroform, it was found that addition did not take place rapidly since even the first drop of bromine solution decolorized slowly. This is characteristic of stable acids in general, and is a definite proof that the labile acid (Δ^3 -dihydronaphthoic acid-2) from which the new isomer had been prepared is absent, since the latter decolorizes bromine instantaneously. The reactions of the dibromides of the three isomers, however, give even more conclusive proof than that above. The evidence from this source is presented in one of the following sections.

Finally, known mixtures of the 118° isomer with the 101° isomer, the 161° isomer and with β -naphthoic acid, respectively, were prepared and it was found possible to secure fairly satisfactory separations by means of fractional precipitation.

The 118° isomer crystallizes from dilute acetic acid or from dilute alcohol in clusters of radiating needles. Its degree of solubility in water, dilute acetic acid, ligroin, etc., is intermediate between that of the two other isomers. Preliminary measurements of the ionization constant of the 118° isomer have indicated that the value for this constant is very close to 3.0×10^{-5} at 25° in aqueous solution.

Solubility in Water of the 161° and 118° Isomers.—The stable acid (161°) described by Sowinski¹ and by Baeyer¹ is more stable toward melting point, solubility and ionization than is the new isomer described above. Toward rearrangement, however, the 118° acid is the most stable isomer under the conditions discussed above. These measures of stability are not necessarily contradictory since they are determined under widely varying conditions. The solubilities of the two isomers in pure water at various temperatures were determined and it was found that the solubility curves do not intersect in the range examined. This solubility data is given in the following table. In order to make direct comparison possible, the results are expressed in terms of 10 cc. of the saturated solution. The amounts actually titrated were larger and at the lower temperatures amounted to 50 cc. The temperature coefficient

¹ *Loc. cit.*

of solubility for the two isomers is almost identical for the range 0° to 97° . This explains the difficulty found in completely separating these two acids.

TABLE III.

Temp.	No. of cc. saturated solution.	No. of cc. 0.01 N Ba(OH) ₂ solution used.	
		118° isomer.	161° isomer.
96-97°	10.00	20.1	10.5
90°	10.00	14.6	8.0
80°	10.00	9.3	4.68
71-72°	10.00	6.7	3.48
55-56°	10.00	2.89	1.45
40°	10.00	1.34	0.69
20°	10.00	0.56	0.34
0°	10.00	0.39	0.19

Preparation of the Amides.—The amides of the three dihydro acids and of the tetrahydro acid were prepared as directed under the section dealing with β -naphthoic acid. To test out the method for unsaturated acids, the amide of cinnamic acid was prepared. The melting points have been given in Table II.

Preparation of the Dibromides.—The method used was similar to that recommended by Nef¹ for the preparation of the dibromide of cinnamic acid. Three grams of the 118° isomer are dissolved in 10 cc. chloroform. To the clear, colorless solution there are added slowly 3 g. of bromine dissolved in 5 cc. of chloroform, the solution being kept cold. (Besemfelder² used almost 100% excess bromine.) The sparingly soluble dibromide begins to separate out after fifteen minutes. The mixture is, however, allowed to remain in a dark place for two hours, after which only a faint bromine color remains; it is then filtered, using a suction filter and the crystals washed with 10 cc. chloroform. White crystals melting at 190° . Yield, 5 g. For the determination of the melting point and for the analysis, a product which had been precipitated from a more dilute chloroform solution was used.

Subst., 0.1956; AgBr, 0.2219. Calc. for $C_{11}H_{10}O_2Br_2$: Br, 47.9%. Found: 48.2%.

The dibromides of the labile (101°) acid and of the stable (161°) acid were prepared in an analogous manner; in each case the dibromides were found to be less soluble in chloroform than the corresponding acids and for this reason they were readily obtained pure. Their melting points have been given in Table I. No difficulty was found in preparing the dibromide of the labile acid since it did not decompose spontaneously as reported by Baeyer and Besemfelder. Its analysis is as follows:

Subst., 0.2449; AgBr, 0.2755. Calc. for $C_{11}H_{10}O_2Br_2$: Br, 47.9%. Found: 47.8%.

¹ *Ann.*, 308, 267 (1899).

² *Loc. cit.*, pp. 190 and 194.

Reactions with Alkalis of the Three Isomeric Dibromides.—The dibromide of the labile acid (Δ^3 -dihydronaphthoic acid-2) dissolves completely in 5% sodium carbonate solution. Soon, however, the clear solution becomes turbid and a precipitate is formed which increases rapidly. The product formed was found to be the monobromolactone already described by Baeyer. One gram of the bromide yielded 0.6 g. (80%) of the lactone. The melting point after recrystallization was 126°. The fact that the initial product dissolves completely in dilute sodium carbonate, proves that the lactone is not present as a contamination of the dibromide. When this lactone was boiled with 20% potassium hydroxide solution, it dissolved slowly and remained in solution after cooling. The following day the solution was acidified, an acid being thrown down which melted after one crystallization from water at 143–45° and whose solubility in water is 1.5 g. per liter. From the method of preparation, this product was suspected of being a keto acid. This agrees with its neutral equivalent, its analyses and with the fact that it readily forms a semicarbazone. (M. p. 266° decomp.) It is fairly stable toward the action of potassium permanganate in the cold.

0.0977 g. acid required 6.85 cc. KOH solution 0.0764 *N*.

Neutral equivalent = 187. Theoretical for keto acid = 190.

Subst., 0.0772; CO₂, 0.1964; H₂O, 0.0367. Required for C₁₁H₁₀O₃: C, 69.47%; H, 5.31%. Found: 69.35%, 5.28%.

The dibromide of the 161° stable acid (Δ^2 -dihydronaphthoic acid-2), when dissolved in 5% sodium carbonate solution or in 5% potassium hydroxide solution, decomposed smoothly, with the loss of two molecules of hydrobromic acid, into β -naphthoic acid. Boiling the bromide with alcoholic potassium hydroxide solution is unnecessary since the decomposition proceeds rapidly in aqueous solution even at 0°. From 0.4 g. of bromide, 0.19 g. (90%) of pure β -naphthoic acid was obtained. This reaction agrees¹ with that observed when the dibromide of Δ^2 -dihydronaphthoic acid-1 is treated with alkali.

The bromide of the 118° isomer (Δ^1 -dihydronaphthoic acid-2) was treated with cold 5% aqueous potassium hydroxide and the decomposition of the product followed by drawing off small portions of the solution at intervals. It was found that most of the bromide decomposed during the first minute, and that the reaction was complete in less than fifteen minutes. The color changes described previously take place on warming the solution, but titration showed that no additional amount of alkali was required. The trace of indifferent substance already mentioned in the theoretical part of this paper was separated by ether extraction from alkaline solution. It was a liquid possessing a fragrant odor and still contained bromine. Because of the small quantity formed in the reaction, it was not further examined.

¹ Kamm and McClugage, *THIS JOURNAL*, 38, 419 (1916).

The main product formed is a dihydroxy acid. Because of the great solubility of the latter, it was separated from the acidified solution by repeated ether extractions. The fact that its solubility in ether is not great necessitates ten to fifteen extractions. It separates from the ether in white plates. From 3 g. of the dibromide, 1.2 g. (65%) of the dihydroxy acid was isolated. M. p. 182° .

0.0370 g. required 6.15 cc. $\text{Ba}(\text{OH})_2$ solution 0.0281 *N*. Neutral equivalent found, 214. Theory, 208. Subst., 0.0780; CO_2 , 0.1808; H_2O , 0.0415. Theory for $\text{C}_{11}\text{H}_{12}\text{O}_4$: C, 63.46%; H, 5.82%. Found: 63.20%, 5.91%.

The structure of this dihydroxy acid is further demonstrated by the fact that under the conditions outlined below, it was oxidized to *o*-carboxyhydrocinnamic acid of known structure.

The reaction observed in the decomposition of the bromide of Δ^1 -dihydronaphthoic acid-2 agrees with that of the bromides of Δ^1 -tetrahydrobenzoic acid and of Δ^1 -dihydronaphthoic acid-1.

Purity of the Dibromides.—The reactions described above and also in the theoretical part of this paper may be used to test the purity of a given dibromide, in the following manner: The dibromide of Δ^2 -dihydronaphthoic acid-2 is decomposed into the monobromolactone as described, and the latter separated by ether extraction. No acid is precipitated upon acidification of the alkaline solution. This shows that no trace of the dibromide of Δ^2 -dihydronaphthoic acid-2 could have been present since the latter decomposes almost quantitatively under these conditions into the extremely insoluble β -naphthoic acid. Similarly, the dibromide of Δ^1 -dihydronaphthoic acid-2 does not yield a trace of β -naphthoic acid. Neither could the monobromolactone of the Δ^2 -isomer be detected. Hence the dibromide of the Δ^1 -isomer must be free from the other two isomers.

Recovery of Dihydro Acids from the Bromides.—The three dihydro acids may be recovered from the corresponding bromides by treating the latter with zinc dust in glacial acetic acid. This method was found efficient as a means of purification and as a proof of the homogeneity of a given acid. This has already been described in detail in the section on the preparation of the labile dihydro- β -naphthoic acid.

Oxidation of Δ^1 -Dihydronaphthoic Acid-2. Proof of Structure.—The method used by Besemfelder¹ in attempting to isolate a definite oxidation product from the Δ^2 -isomer was the addition of potassium permanganate in excess until a permanent color was obtained. Consequently a large excess of permanganate was used (17 g. for 4 g. of the dihydro acid). In the present work, the following modification was adopted: The calculated amount of potassium permanganate was added slowly

¹ *Loc. cit.*

to the ice-cold solution of dihydro acid dissolved in a very dilute alkali. In spite of these precautions, the only definite product isolated in several preliminary oxidations was *o*-phthalic acid or a mixture of acids consisting chiefly of the latter. The method finally used was to carry on the oxidation in steps using about the theoretical amount (or 10% excess) of the oxidizing agent necessary to carry the oxidation to a given stage.

Five grams of the 118° acid are dissolved in 75 cc. water containing 3 g. KOH and the solution cooled with ice. For the oxidation, 6 g. of KMnO_4 dissolved in 500 cc. water are added slowly during a period of about one hour, the solutions being kept cold. Finally, the mixture is warmed on the water bath to coagulate the manganese dioxide. The latter is filtered off, using suction, and the filtrate evaporated down to about 100 cc. The yellow solution is then again filtered if necessary and acidified. After standing overnight, the oxidation product will have separated in the form of radiating clusters. An additional yield is obtained by ether extraction, bringing the total to 50–60% of theory. One recrystallization from water and treatment with bone-black yields a white product melting at 119–120°. In comparison with the dihydro acid from which it is derived, it is very soluble in water. The oxidation was repeated several times in the attempt to isolate the intermediate dihydroxy acid, but uniformly the results outlined above were obtained.

0.0462 g. acid required 10.50 cc. NaOH 0.0210 *N*. Neutral equivalent found = 210. Subst., 0.1054; CO_2 , 0.2340; H_2O , 0.0566. Required for $\text{C}_{11}\text{H}_{10}\text{O}_4$: C, 64.04%; H, 4.90%; for $\text{C}_{11}\text{H}_{10}\text{O}_4 + \text{H}_2\text{O}$: C, 58.9%; H, 5.40%. Found: 60.5%, 5.98%.

This product is believed to be the keto hydroxy acid or its hydrate indicated in the theoretical part of this paper. The titration value is not conclusive except that it shows that we are not dealing with the predicted dibasic keto-acid which would have a neutral equivalent of only 111. In a case of this kind, the titration is more conclusive than is the elementary analysis. The above product is suspected of being the keto hydroxy acid with water of crystallization. The neutral equivalent of a sample soon after crystallization, having been dried on a clay plate for one hour, gave a value of 230. The initial product had been standing for several days. Several unsuccessful attempts were made to prepare a semicarbazone.¹

The keto-hydroxy acid may be further oxidized to *o*-carboxy hydrocinnamic acid under the conditions outlined above (5 g. acid require 5 g. KMnO_4). In this case it is noticed that the permanganate is not decolorized as rapidly as in the oxidation of unsaturated acids. The oxidation product is isolated as in the previous experiments, and is obtained almost pure, melting at 164°. One recrystallization and treatment

¹ Discussion of steric hindrance in semicarbazone formation. Kötze and Michels, *Ann.*, 350, 208–9 (1906).

with a small quantity of bone-black gave a 40% yield of a pure white crystalline product melting at 165.5°.

0.052 g. of acid required 24.8 cc. NaOH 0.0210 *N*. Neutral equivalent found = 100. Theory, 97. Subst., 0.1424; CO₂, 0.3220; H₂O, 0.0644. Required for C₁₀H₁₀O₄: C, 61.85%; H, 5.19%. Found: 61.67%, 5.03%.

This data proves that the oxidation product is *o*-carboxyhydrocinnamic acid.

An attempt was made to oxidize the dihydroxy acid obtained from the dibromide of Δ^1 -dihydronaphthoic acid-2 to the keto hydroxy compound (m. p. 119–120°). This was, however, not successful, although some *o*-carboxyhydrocinnamic acid was obtained, which serves to demonstrate the structure of the dihydroxy acid.

Summary.

1. The missing isomeric dihydro- β -naphthoic acid has been prepared by rearrangement of both Δ^1 -dihydronaphthoic acid-2 and Δ^2 -dihydronaphthoic acid-2 and its identity as a chemical individual has been established.
2. The structures of the three isomeric dihydro acids have been demonstrated through the reactions of the corresponding dibromides.
3. The structure of Δ^1 -dihydronaphthoic acid-2 (the new isomer) has been conclusively established by means of oxidation reactions.

URBANA, ILL.

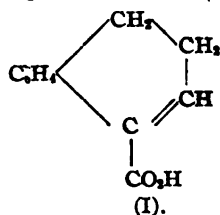
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF ILLINOIS.]

THE STRUCTURE OF THE DIHYDRO- α -NAPHTHOIC ACIDS.

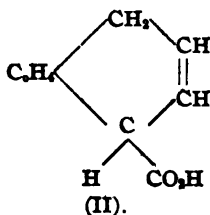
BY OLIVER KAMM AND HARRY BRUCE MCCLUGAGE.¹

Received December 18, 1915.

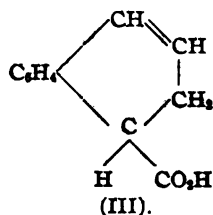
Three dihydro- α -naphthoic acids having the unsaturated linkage in the ring carrying the carboxyl group are theoretically possible, *viz.*:



Δ^1 -Dihydronaphthoic acid-1.



Δ^2 -Dihydronaphthoic acid-1.



Δ^4 -Dihydronaphthoic acid-1.

Of the above acids, two have previously been prepared although the structure of only one of them has been conclusively established. In the present paper additional evidence is presented in favor of the struc-

¹ From a thesis presented to the Faculty of the University of Illinois in partial fulfilment of the requirements for the degree of Bachelor of Arts (McClugage, 1915).

tures of the two known isomers. Although we have not yet succeeded in synthesizing the third isomeric acid, it seems desirable to publish our results at the present time because of the fact that the reactions used for the demonstration of structures in the α -naphthoic acid series are exactly analogous to those used by Derick and Kamm¹ in the beta series. This evidence, together with the analogy found in the benzoic acid series, furnishes strong proof that the reactions outlined below may be used for the demonstration of structure of these unsaturated acids.

The reduction products of the naphthoic acids were studied almost simultaneously by Sowinski² and by Baeyer and Schoder,³ who prepared two of the dihydro acids. The labile acid (so named because of the ease of its rearrangement into the higher melting stable isomer) was prepared by the direct reduction of α -naphthoic acid with sodium amalgam. The stable isomer was obtained by boiling the labile acid in aqueous sodium hydroxide solution.

The evidence in favor of Structure I (Δ^1 -dihydronaphthoic acid-1) for the stabile dihydro acid is based mainly upon the fact that by its oxidation Baeyer and Schoder were able to obtain an acid melting at 165°, which agrees with the melting point of *o*-carboxyhydrocinnamic acid. To the above evidence must be added the generalization presented by Baeyer: In a rearrangement of a labile acid under the influence of an alkali the double union shifts toward the carboxyl group.

The labile dihydro acid may therefore have either of the two remaining structures. Meyer and Jacobson⁴ state that either Structure II or III may be the correct one for this acid, but from the data available they have not attempted to differentiate between these two formulas. Sowinski,⁵ without conclusive evidence in his favor, has presented Formula III, while Bethmann,⁶ who has measured the ionization constants of the dihydro acids, also presented a Δ^2 -structure for one of the isomers. Baeyer,⁷ on the other hand, is inclined in favor of Structure II. The evidence advanced in this paper agrees with the views of Baeyer.

The labile dihydro acid has been resolved into its optically active components by Pickard and Neville.⁸ This is, however, not a demonstration of the structure of the acid since both Δ^2 -dihydronaphthoic acid-1 and Δ^3 -dihydronaphthoic acid-1 possess asymmetric molecules. Consequently Pickard and Neville have attempted to decide between the

¹ Preceding article in THIS JOURNAL.

² *Ber.*, 24, 2354 (1891).

³ *Ann.*, 266, 169 (1891).

⁴ "Lehrbuch der Organischen Chemie," 1903, Vol. 2, Pt. 2, p. 446.

⁵ *Loc. cit.*, p. 2360.

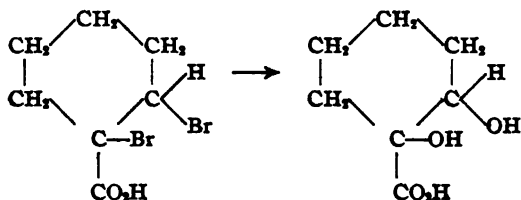
⁶ *Z. physik. Chem.*, 5, 400 (1890).

⁷ *Loc. cit.*, p. 173.

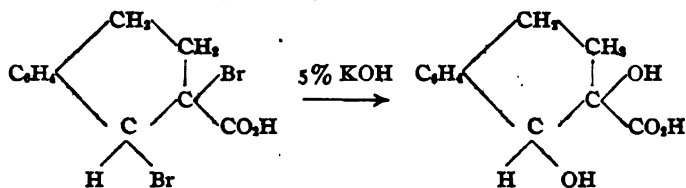
⁸ *J. Chem. Soc.*, 87, 1763 (1905).

two possible formulas by studying the speed of rearrangement of the labile into the stable isomer. For this purpose, the *d*-form of the labile acid was used, since it was possible to follow the rearrangement into the inactive stable isomer by means of polarimetric measurements. They state in their conclusions that it is some additional evidence in favor of the Δ^2 -constitution that the measurements of the velocity of the transformation into the Δ^1 -acid show the rearrangement to be unimolecular, but that it must be remembered that what is measured may be the velocity of the slower of two successive changes. This, therefore, was not advanced as a final proof of the structure of the labile acid.

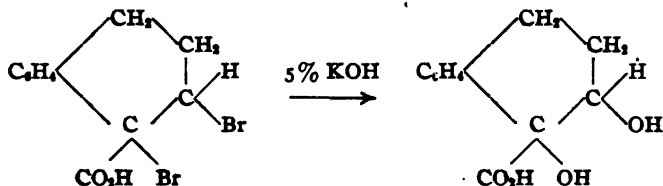
In the present work the evidence in favor of the structures of these dihydro acids is based upon the reactions of the corresponding dibromides with cold, dilute, aqueous solutions of alkalis. When the dibromide of Δ^1 -tetrahydro benzoic acid was treated with dilute alkali solution, Aschan¹ found that the two bromine atoms were replaced by hydroxyl groups.



Similarly, it was found² that the bromide of Δ^1 -dihydronaphthoic acid-2 reacts in an exactly analogous manner.



An exact analogy was found to exist between the above reactions and that of the dibromide of the stable dihydro- α -naphthoic acid, since the latter was converted into the dihydroxy acid upon treatment with a five per cent. potassium hydroxide solution. No evidence was obtained of the formation of α -naphthoic acid which, because of its slight solubility

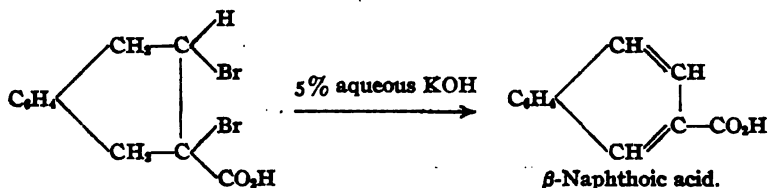


¹ *Ann.*, 271, 281 (1893).

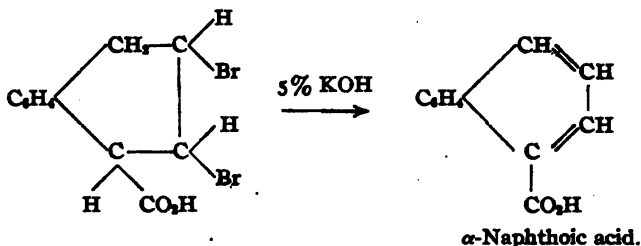
² Derick and Kamm, *Loc. cit.*

in water, would have been detected even in traces. This is, therefore, an argument in favor of the Δ^1 -structure.

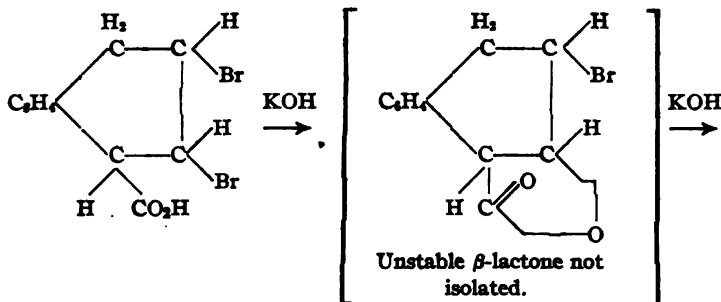
If the labile dihydro acid possesses Structure II above, we are able to predict the reactions of its dibromide by analogy to previously observed reactions. For example, in the case of the dibromide of Δ^2 -dihydro-naphthoic acid-2, the reaction forming β -naphthoic acid is almost quantitative.¹



By analogy one would predict that the dibromide of the dihydro- α -naphthoic acid possessing Structure II would react in the following analogous manner:

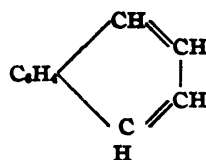


When the dibromide of the labile acid was treated in the cold with dilute aqueous potassium hydroxide solution, an exceptionally good yield of α -naphthoic acid was obtained. This reaction is not quite quantitative, due to the formation of a trace of naphthalene, according to the following reactions:²



¹ See the preceding article on the structure of the dihydro- β -naphthoic acids.

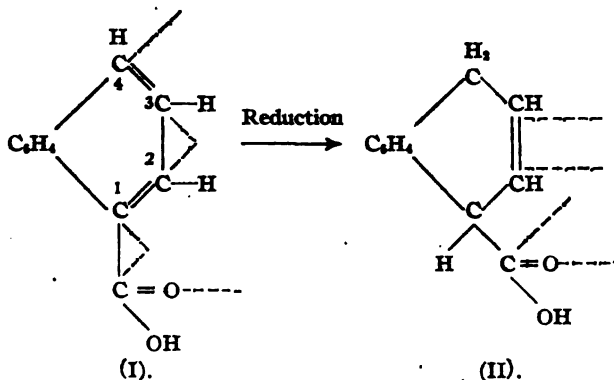
² This side reaction, as will be shown in the experimental part of this paper, explains the conflicting data (Baeyer and Schoder vs. Sowinski) concerning the reaction of this bromide with dilute alkali.



Naphthalene.

The formation of α -naphthoic acid from the dibromide of the labile acid has been reported by Schoder, who conducted his experiment with the use of warm alcoholic potash, conditions under which the dibromide of the stable acid also yielded α -naphthoic acid.¹ In the present work, however, conditions were similar to those referred to above in the β -naphthoic acid series, conditions under which the bromide of Δ^1 -dihydronaphthoic acid-1 yielded no α -naphthoic acid.

From the above data we conclude that Structure II is the correct one for the labile dihydro acid. Additional evidence in favor of this formula is offered by Thiele's Partial Valence Theory,² which predicts the first dihydro- α -naphthoic acid formed by reduction to be the Δ^2 -isomer. According to Thiele's view, the formulas for α -naphthoic acid and its first reduction product would be represented as follows:



Since the valence on carbon 4 (Formula I) would be only partly conjugated with the phenyl ring, the formula predicts that the first two hydrogen atoms would add in the 1,4 positions, the double union shifting to the 2,3 position. Exact analogies to the above reaction have been reported by Baeyer in the reduction of terephthalic acid, $\Delta^{1,2}$ -dihydroterephthalic acid, and others; in fact some of the strongest evidence in favor of the Thiele views are to be found throughout the classical work of Baeyer on the "Constitution of Benzene."³

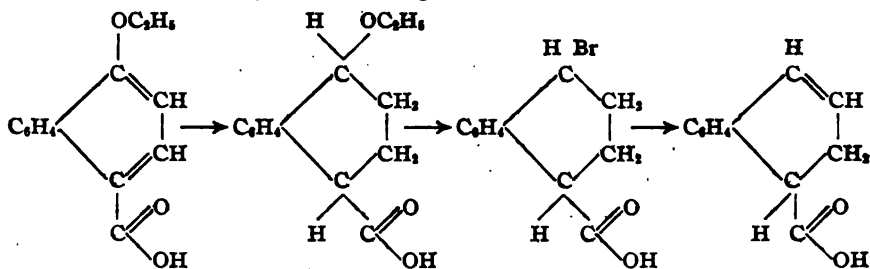
¹ *Ann.*, 266, 183 (1891).

² *Ibid.*, 306, 125 (1899).

³ For brief discussions see Cohen's "Organic Chemistry for Advanced Students," 1910, pp. 448-456; Henrich "Theorien der Organischen Chemie," 1912, pp. 36 and 64.

The product obtained by the rearrangement of the labile isomer (Δ^2 -acid) is Δ^1 -dihydronaphthoic acid-1. We have examined the products of rearrangement in the hope of being able to isolate at least traces of the Δ^2 -acid. Up to the present time, however, this search has not been successful.

An attempt was also made to synthesize the third isomeric dihydro acid (Δ^2 -dihydronaphthoic acid-1). The method chosen for this synthesis is illustrated by the following series of reactions:



When the 1,4-ethoxy naphthoic acid was treated in hot solution with sodium amalgam, the reduction was carried to completion but the ethoxy group was also replaced by a hydrogen atom, tetrahydro- α -naphthoic acid being the product obtained. It is hoped that by reduction in the cold this elimination of the ethoxy group can be prevented.

A similar observation has been reported by Einhorn and Lumsden,¹ who found that *o*-ethoxy benzoic acid when reduced yields hexahydrobenzoic acid in place of the desired ethoxy derivative.

Experimental Part.

The Preparation of α -Naphthoic Acid.—This acid was prepared through the nitrile, the latter having been prepared from α -naphthylamine by the Sandmeyer reaction. The nitrile, together with some naphthol, was separated by means of steam distillation. The distillate was treated with alkali and the nitrile removed by ether extraction.

In the hydrolysis of the nitrile the reaction was carried to the intermediate amide stage by using a solution of alcoholic potash prepared from 99% alcohol. The amide partly crystallized out from the alcohol solution and the remainder was obtained by dilution with water. The melting point was found to be 205° and did not change on further recrystallization.²

Hydrolysis to the acid stage was accomplished by boiling either the nitrile or the amide with a mixture of equal volumes of water, glacial acetic acid and sulfuric acid (sp. gr. 1.84) for about one hour. The acid was ob-

¹ *Ann.*, 286, 264 (1895).

² The melting points given in this paper refer to capillary melting points, corrected for stem exposure. The corrections were usually negligible since calibrated Anschütz thermometers were used.

obtained by pouring the above hydrolysis mixture into cold water. The product was almost colorless and after one crystallization from 30% acetic, was found to melt at 162° . This melting point checked exactly with the one obtained from the purified Kahlbaum product. The yield was less than 20% of the theoretical.

α -Naphthoic acid was also prepared from the bromide of Δ^2 -dihydronaphthoic acid-1 by the method described in one of the following sections. The melting point of this product after one crystallization from dilute acetic acid was found to be 161° , but a second purification raised the value to 162° .

Preparation of the Labile Dihydro- α -naphthoic Acid.— α -Naphthoic acid was reduced with sodium amalgam, a stream of carbon dioxide being passed into the solution to neutralize the free alkali, as directed by Baeyer and Schoder.¹ For a 10 g. portion of the acid, 200 g. of 3% sodium amalgam were used. At a temperature of about 10° , the reduction to dihydro acid was complete in about thirty minutes, as was indicated by the permanganate test.

The dihydro acid, isolated and purified according to the method given by the above authors, was found to melt sharply at 86° . Because of this variation from the reported value 91° , and in the hope that some Δ^2 -dihydronaphthoic acid-1 had been formed as one of the products in the reduction, we have taken special precautions in the purification of the product.

The acid obtained from the reduction of two 10 g. portions of α -naphthoic acid and including the product obtained from the mother liquors by ether extraction, was divided by fractional precipitation² into nine approximately equal fractions. A final fraction (0.6 g. in weight) was obtained by means of ether extraction. With the exception of the first fraction, which was slightly colored, all fractions were pure white. Fractions 2 to 9 all melted at $83-4^{\circ}$ and after one crystallization from petroleum ether melted at about 85° . The fraction obtained by ether extraction melted two degrees lower.

Since the labile acid is the most soluble acid in this series, and since it also possesses the largest ionization constant, we would in the case of fractional precipitation of a mixture find it in highest purity in the end fractions. Consequently we have repurified separately Fraction No. 2 and Fraction No. 9, by four successive recrystallizations from petroleum ether.

Fraction No. 2. M. p.		Fraction No. 9. M. p.	
1.....	84°	1.....	84°
2.....	85.5°	2.....	85.5°
3.....	86°	3.....	86°
4.....	86°	4.....	86.5°

¹ *Loc. cit.*

² See preceding article for other applications of this method.

After one recrystallization from dilute acetone the melting point 86.5° was not changed. Immediately following the above observations the thermometers used were tested out both at the boiling points of pure benzene and of water and found to be accurate.

The question therefore arises: Is the above acid, which was purified more highly than has been reported previously, identical with the acid (m. p. 91°) prepared by Baeyer and Schoder?

A sensitive criterion of the purity of this acid is rendered available by a measurement of its ionization constant. Fortunately, Bethmann¹ has measured the ionization constants of these acids, using in his work the samples prepared by Schoder. Unfortunately, however, he does not report the melting points of the acids and does not state whether the samples received any additional purification.

Ionization Constants of the Dihydro- α -Naphthoic Acids.—The ionization constants of both the labile and the stable dihydro- α -naphthoic acids were determined in aqueous solution at a temperature of 25° . The details of the conductivity work will be presented in a subsequent paper from this laboratory. In the calculation of the constants the value for the conductivity at infinite dilution ($\lambda_0 = 376$) was calculated from the Ostwald rule.² In the following tables

C = concentration of the acid.

λ = equivalent conductance at 25° at the concentration C, uncorrected for the conductivity of the water used.

K = ionization constant calculated according to the equation

$$K = \frac{C\lambda^2}{\lambda_0(\lambda_0 - \lambda)}.$$

TABLE I.—LABILE ACID.*

Δ^2 -Dihydronaphthoic acid-1.

M. p. 86.5° . Water used = 0.84×10^{-6} . M. p. 121.5° . Water used = 0.65×10^{-6} .

C.		λ .	$K_a^{25^{\circ}}$.
0.004	N	59.02	11.69×10^{-5}
0.002	N	80.30	11.60×10^{-5}
0.001	N	107.80	11.52×10^{-5}
0.0005	N	141.85	11.43×10^{-5}

TABLE II.—STABLE ACID.

Δ^1 -Dihydronaphthoic acid-1.

M. p. 121.5° . Water used = 0.65×10^{-6} .

C.		λ .	$K_a^{25^{\circ}}$.
0.001	N	92.19	7.96×10^{-5}
0.0005	N	122.66	7.90×10^{-5}
0.00025	N	159.47	7.81×10^{-5}

The values given by Bethmann, uncorrected for changes in units, are as follows:

$K_a^{25^{\circ}}$ Labile dihydro- α -naphthoic acid = 11.4×10^{-5} ;

$K_a^{25^{\circ}}$ Stable dihydro- α -naphthoic acid = 8.1×10^{-5} .

The agreement with the values found in the present work is satisfactory enough to demonstrate that the acids were practically identical with those studied by Baeyer and Schoder.

¹ *Z. physik. Chem.*, 5, 399 (1890).

² See Lunden's "Affinitätsmessungen an Schwachen Säuren und Basen," p. 9.

Preparation of the Stable Dihydro- α -naphthoic Acid.—In the preparation of this acid by the rearrangement of the labile dihydro acid it is not necessary to boil the latter with dilute alkali for several hours. We find that a thirty-minute treatment with boiling 5% aqueous potassium hydroxide solution is sufficient to secure a complete rearrangement. Since the melting point of this acid was found to differ from the reported value the method of purification is mentioned here in detail.

Baeyer and Schoder¹ state that the crude acid melts at 115° before and 125° after recrystallization. The solvents used were water and ethyl acetate.

In the present work the acid was purified as follows:

(a) The acid obtained by rearrangement was precipitated in fractions, each fraction melting at about 120°, thus showing the product to be free from the labile isomer since the latter would appear in the end fractions.

(b) Each individual fraction was then recrystallized from ethyl acetate, and the melting points found to be 121°.

(c) The above fractions melting at 121° were then converted into the bromide, the latter purified, and the free dihydro acid recovered and crystallized from dilute acetic acid. The melting point was still 121°.

(d) This acid recovered from the dibromide was then subjected to fractional precipitation with the following results:

No. of fraction.....	1	2	3	4	5
Melting point.....	120°	121°	121°	121°	121°

(e) Fractions 2 to 5 were combined and recrystallized successively from dilute acetic acid, dilute acetone and finally from low-boiling ligroin. *M. p.* 121.5°.

The ionization constant of this acid (*m. p.* 121.5°) has been measured as a test of its purity, the result being given in Table II (p. 426).

Preparation of the Dibromides.—Five grams of the labile acid were dissolved in 10 cc. of chloroform and a solution of 5 grams of bromine, diluted with about 5 cc. chloroform added gradually. Decolorization of the bromine was rapid and since the solution was kept cold the evolution of hydrobromic acid was very slight. The bromine addition product is in this case soluble in chloroform and therefore it was necessary to precipitate it by the addition of several volumes of petroleum ether. The derivative separated at first in the form of an oil which upon manipulation with a stirring rod was converted into a finely divided white crystalline solid, which was filtered off and washed with ligroin. The yield was 6.5 g. and the *m. p.* 125°, although the latter value was slightly raised upon subsequent purification.

The bromide of the stable dihydro acid was prepared in a similar manner, except that because of the fact that it is only slightly soluble in chloro-

¹ *Ann.*, 266, 181 (1891).

form it could be isolated exactly as described for the bromides of the three dihydro acids in the β -naphthoic acid series. The theoretical amount of bromine was dissolved in 5 cc. chloroform and the solution added gradually to a cold solution of 5 grams of the stable dihydro acid dissolved in 20 cc. chloroform. The bromine color was destroyed less rapidly than in the preceding experiment. After the solution had been standing in a dark place for about fifteen minutes the bromide had separated almost completely. The cream colored solid was filtered off and washed with a small quantity of chloroform. The final product was almost pure white and melted at 151° with decomposition. The yield was 7.6 grams.

Decomposition with Alkali of the Dibromide of the Labile Acid.—When the dibromide derived from the labile dihydro- α -naphthoic acid was treated with dilute alkali (5% aqueous potassium hydroxide solution was used) it dissolved completely to give a clear solution. After about one minute, however, the solution became slightly turbid, due to the separation of a small amount of naphthalene. This product was filtered off and its melting point found to be 79° . From the filtrate, an 85% yield of pure α -naphthoic acid was obtained.¹ The melting point of the product after one crystallization from dilute acetic acid was 161° . The above data probably explains the discrepancies between the observations of Sowinski and those of Baeyer and Schoder, since the former states that the dibromide is not completely soluble in alkali, while the latter disagree with this statement and claim that a clear solution in alkali is obtained.

The rate of decomposition of the dibromide with 5% aqueous potassium hydroxide solution at room temperature (about 25°) is extremely rapid as is indicated by the following table. A weighed quantity of the dibromide was dissolved in a known volume of standardized alkali and 1 cc. portions withdrawn at definite time intervals, the excess of alkali being determined by adding a known excess of standard acid and titrating back to color (using phenolphthalein) with standard alkali. Table III shows that most of the dibromide is decomposed during the first five minutes and that the decomposition is complete after fifteen minutes. The total amount of alkali used corresponded very closely with the theoretical amount for the elimination of two molecules of hydrobromic acid. The correction for the amount of alkali neutralized by the carboxyl group has, of course, been applied to the figures given in Table III:

TABLE III.

Total time of reaction.....	0	5	15	30 min.
No. of cc. of 0.01 <i>N</i> KOH required.....	0.0	22.4	35.6	35.6 cc.

¹ Sowinski's statement that a mono bromo derivative of a dihydro acid is obtained under these conditions was not confirmed since it was found, by conducting the experiment with a standard alkali solution, that exactly two molecules of hydrobromic acid were eliminated. It is probable that Sowinski obtained a mixture of dibromo acid, α -naphthoic acid, and the mono bromo derivative.

From the dibromide, the original dihydro acid was recovered by means of glacial acetic acid and zinc dust. By use of the same method Schoder obtained a product melting at 85° .

Decomposition with Alkali of the Dibromide of the Stable Acid.—Three grams of the dibromide were dissolved in 60 cc. of approximately 5% aqueous potassium hydroxide solution. The liquid soon assumed a light purple color which in the course of one-half hour changed to a wine-red. Upon acidification, the color of the solution changed to yellow. The colored product is acidic in nature for it may be extracted with ether only after the alkaline solution has been acidified. It was separated from the dihydroxy derivative described below, by means of its greater solubility in ether.

The acid solution was extracted repeatedly with ether; extractions 1 and 2 were set aside because of the presence of the colored impurity mentioned above, while extractions 3 to 10 were combined, dried with anhydrous sodium sulfate, and the ether evaporated for the isolation of any water soluble acid present. The acid crystallized from the ether solution, after partial evaporation of the latter, in the form of white plates. (Melting point 175° d.) The acid is only sparingly soluble in ether but very soluble in water, which agrees with the properties of a hydroxy acid. Its aqueous solution does not reduce potassium permanganate solution instantly, as is the case with the unsaturated acids. Its neutral equivalent was determined with the following results:

0.0381 g. of substance required 8.80 cc. of 0.0207 *N* NaOH. Neutral equivalent found = 209. Theory for $C_{11}H_{12}O_4$ = 208.

Subst., 0.1476; CO_2 , 0.3364; H_2O , 0.0782.

Theory for $C_{11}H_{12}O_4$: C, 63.46%; H, 5.77%. Found: 62.15%, 5.88%.

The rate of decomposition of the dibromide of the stable dihydro acid was also followed by titration as was described above for the labile isomer. The quantity of alkali used again corresponded closely with the theoretical amount required for the elimination of two molecules of hydrobromic acid, and it was again found that most of the decomposition took place during the first five minutes.

Reduction of 1,4-Ethoxynaphthoic Acid.¹—Five grams of this acid were reduced in hot alkaline solution using 3% sodium amalgam, a stream of carbon dioxide being passed into the solution. The first portion of amalgam (200 g.) reacted quickly, indicating that reduction was taking place. When a small portion of the solution was treated with several drops of dilute potassium permanganate solution instantaneous decolorization took place, indicating partial reduction of the ethoxy acid, since the original product was stable toward permanganate. The total amount

¹ The preparation and proof of structure of this acid will be presented in a later paper from this laboratory.

of 3% amalgam required to complete the reduction was 1200 g. An acid was isolated which was quite stable toward permanganate, as would be expected of a tetrahydro acid. The melting point without special purification was found to be 81° , slightly lower than that of tetrahydro- α -naphthoic acid. Results of the titration for the neutral equivalent were as follows:

0.1390 and 0.0916 g. acid = 9.35 and 6.20 cc. 0.085 *N* alkali. Neutral equivalent found (1) 175 and (2) 174.

The above neutral equivalents agree with the theoretical value (176) for tetrahydro- α -naphthoic acid, indicating that the ethoxy group had been eliminated in the process of reduction.

URBANA, ILL.

ZINGIBEROL—A NEW SESQUITERPENE ALCOHOL OCCURRING IN THE ESSENTIAL OIL OF GINGER.

By BENJAMIN T. BROOKS.

Received November 18, 1915.

It is a well-known fact that the distilled oil of ginger, *Zingiber officinal* Roscoe, possesses the characteristic aroma of ginger. The odor is not intense, but is very persistent, recalling sandal wood oil in this respect. Gildemeister and Hoffman¹ state "Only a few of the important constituents of ginger oil are known; of the substances which give it the characteristic odor nothing is known."

In the course of an examination of ginger oil which had been freed of terpenes and sesquiterpenes, the author isolated and identified citral, methyl heptenone, nonylaldehyde, linalool, *d*-borneol, acetic and caprylic acids, combined as esters, a trace of a phenol which was probably chavicol though not positively identified, cineol and also a sesquiterpene alcohol, $C_{15}H_{26}O$, which evidently bears the same relation to the sesquiterpene, zingiberene, as santalol does to santalene, and since it imparts to ginger oil the peculiar persistent, though mild, ginger odor, I have called it *zingiberol*. Although all of the constituents of ginger oil contribute something to the composite odor of the fresh root, the alcohol zingiberol is the only one of them possessing the peculiarly characteristic fragrance of ginger.

It should, perhaps, be pointed out that ginger oil does not produce the sharp pepper-like sensation when introduced into the mouth that is produced by the fresh root, and that the so-called "gingerol" claimed by Garnett and Greier² to have been isolated by them has no existence in fact. The latter authors did not characterize their gingerol further than that it probably was a phenol and possessed a sharp stinging taste. Fol-

¹ Gildemeister and Hoffman, "Die Aetherische Oele," Leipzig, 2, 292 (1913).

² Chem. Zentr., 1907, II, 924; 1909, II, 1593.

lowing their directions, I isolated from the aqueous alkaline extract, by passing in CO_2 , a very small quantity, about 2%, of oil, consisting of a mixture of the sesquiterpene alcohol zingiberol and a trace of a phenolic substance whose taste was phenolic and suggestive of chavicol.

Zingiberol.

From 150 g. of ginger oil, free from terpenes and sesquiterpenes, there were obtained 41.5 g. of oil distilling from 130° to 160° at 14 mm. pressure. By repeated fractionation, this crude fraction yielded 24 g. of oil boiling from 154° to 157° C. at 14.5 mm. Combustion analysis gave:

	Found. Per cent.		Calculated for	
	I	II	$\text{C}_{15}\text{H}_{24}\text{O}$	$\text{C}_{15}\text{H}_{24}\text{O}$
C.....	80.90	81.54	81.08	81.81
H.....	11.40	11.78	11.71	10.90

The substance is neither a ketone nor aldehyde. Treatment with semicarbazide in the usual manner gave negative results, and an attempt to prepare the oxime resulted in an oil entirely free from nitrogen. Nevertheless, acetylation by heating with acetic anhydride resulted in an oil containing only 17% of ester calculated from the saponification number. Combustion analyses of the acetylated oil also showed that very little dehydration had taken place. Treatment of the substance with phenylisocyanate gave no phenylurethane after standing four days. This fact, together with its behavior to acetic anhydride, indicates that the alcohol is secondary or more probably tertiary. Sodium in dry ether readily forms a sodium compound with the substance, and on gently heating with potassium acid sulfate, water is split off, yielding a hydrocarbon $\text{C}_{15}\text{H}_{24}$, boiling point $255\text{--}257^\circ$, and identical with zingiberene or *iso*-zingiberene. Combustion analysis gave:

Calc. for $\text{C}_{15}\text{H}_{24}$: C, 88.15; H, 11.85. Found: 88.10, 11.41.

Treatment of the hydrocarbon with HCl in glacial acetic acid yielded *iso*-zingiberene dihydrochloride, m. p. 169° .

On treating the alcohol with hydrogen chloride or hydrogen bromide in glacial acetic acid solution and allowing to stand for two days, there are deposited crystals of *iso*-zingiberene dihydrochloride, melting point 169° , or the dihydrobromide, melting point 176° .¹ The dihydrobromide, recrystallized from glacial acetic acid, gave the following analysis:

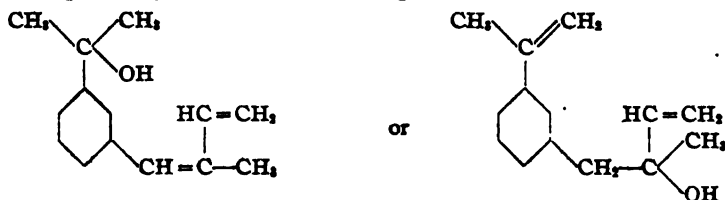
Calc. for $\text{C}_{15}\text{H}_{24}\text{Br}_2$: Per cent. C, 49.18; H, 7.11; Br, 43.71. Found: 49.11; 7.23; 43.73.

Since zingiberol yields a dihydrochloride and a dihydrobromide identical with the dihydrochloride and dihydrobromide, respectively, of the sesquiterpene zingiberene, it is probable that on treating the alcohol with halogen acids a ring formation occurs, as has been shown by Semmler²

¹ Semmler, *Ber.*, 46, 1822 (1913).

² *Loc. cit.*

to be the case with zingiberene. If the constitution advanced by Semmler for zingiberene and *iso*-zingiberene are correct, then the constitution of zingiberol is probably one of the following:



In working with ginger oil, the author was much impressed by the rapidity with which resinification occurs. This is particularly true of the pure hydrocarbon zingiberene, which, as Semmler has shown, contains two conjugated double bonds, as in myrcene and isoprene. The author's experience with both the distillation and extraction of fresh vetiver root, the essential oil of which also consists chiefly of sesquiterpenes and their derivatives, proved that better yields of oil were obtained and that the oil was of much superior quality when the roots were distilled or extracted within a few days of their harvest than after storage several months, as must necessarily be the case with roots shipped to Europe for distillation there. It is highly probable, therefore, that distillation or extraction of the freshly harvested ginger rhizomes would give better oil and in relatively larger yields than the dried material usually employed.

PITTSBURGH, PA.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, THE UPJOHN COMPANY.]

SOME CONSTITUENTS OF SUMBUL ROOT.

BY FREDERICK W. HEYL AND MERRILL C. HART.

Received December 20, 1915.

Since the root of *Ferula Sumbul* is an officially recognized drug of the United States Pharmacopoeia, and has for some years been used as an antispasmodic, it was deemed of interest to subject the root to a more complete chemical investigation. Our present knowledge of its constituents is fairly summarized in the United States Dispensatory¹ where it is stated that the root contains a volatile oil, two balsamic resins, wax, gum, starch, a bitter substance, fat (17%), angelic and valeric acids. Knitl,² with Tschirch, isolated umbelliferon. Cushny³ classifies sumbul with valerian, basing the similarity upon the presence of malodorous volatile oils, which may act psychically and physiologically. Since the oil of sumbul, in consequence of the study of the other constituents re-

¹ U. S. Dispensatory, 19th Ed., 1209.

² Archiv. Pharm., 237, 270 (1899).

³ "Pharmacology and Therapeutics," 73 (1906).

ported in this paper, appears to be important in this connection, we shall report upon it later.

It is generally stated that the musk root now upon the pharmaceutical market in the United States is not true *Ferula sumbul*; but that in its place we have the dried rhizome and root of an undetermined umbelliferous plant, which enters commerce from Central and Northern Asia, through the Moscow drug market. Our sample consisted of the unsliced root imported from Moscow. Further than this it was impossible to trace its origin. The root was of a quality which is now considered official.

The proximate analysis shows that the air-dried root contained 10.2% moisture and 6.5% ash. Ligroin extracted, 11.8%; ether, 14.6%; and alcohol, 27.4%. The residue insoluble in alcohol had the following composition: crude fiber, 17.5%; pentosans, 10.6%; protein, 5.4%; starch, 7.7%; dextrin, 1.4%. The alcoholic extract, which contains the substances entering into pharmaceutical preparations, showed the presence of 1.7% sucrose, approximately 1.0% levulose, and the resin after hot extraction amounts to 18.7%. There is a very considerable discrepancy in the extractive matter removed by alcohol, depending upon the temperature. Whereas boiling 95% alcohol extracted 27.4% of sumbul root, the cold percolation which was exhaustively completed, extracted only about 20%, and about 17.3% was precipitated by the addition of water.

The products present in the alcoholic solution (obtained by cold percolation) and soluble in water besides the sugars above mentioned, are acetic acid, a glucoside of umbelliferon, and betaine.

The resin insoluble in water, which forms the most conspicuous portion of this drug, was extracted successively with ligroin, ether, chloroform, ethyl acetate, and alcohol.

The ligroin extract consisted to the extent of about 17% of resinous material other than fat. This product was a white acid resin, soluble in one per cent. potassium hydroxide, and yielded upon hydrolysis vanillic acid and an oil resembling the volatile oil. The fat yielded a large amount of indefinite unsaponifiable material, of which one fraction showed a constant boiling point at 168–173° at 12 mm. and upon analysis gave values indicating the formula $C_{15}H_{18}O$. The unsaponifiable matter further yielded a phytosterol, $C_{27}H_{46}O$, melting at 134–135°. The corresponding acetate melts at 121–122°. The following fatty acids were identified: acetic, butyric, valerianic, tiglic, angelic, oleic, linoleic, cerotic, palmitic and stearic acids.

The ether extract of the resin, yielded a phytosterolin, $C_{28}H_{48}O_6$, melting at 290°. It formed an acetate that melted at 159–160°. A trace of vanillin was indicated by color tests. The ether extract consists of neutral resinous (42%) and acidic resinous (52%) constituents. The former proved to be an ester, and yielded umbelliferon and therefore

belongs with the group that includes galbanum, sagapen and asafoetida. The acidic resin could be prepared as an almost white powder, but fractional extraction indicated this to be a mixture of resin acids. These acids upon hydrolysis yield both vanillic acid and umbelliferon.

The chloroform extract of the resin consisted largely of a resinous glucosidic substance. It yielded umbelliferon and glucose upon hydrolysis.

The product extracted from the resin with ethyl acetate was not glucosidic but umbelliferon was prepared from it after hydrolysis.

The alcoholic extract of the resin also yielded umbelliferon and a reducing sugar upon hydrolysis.

Experimental.

A. Proximate Analysis (By Mr. J. F. Staley).—A sample of the air-dried root after grinding and sieving was quantitatively extracted with various solvents and the following results were obtained:

Extract.	Per cent.
Ligroin (35–55°).....	11.72, 11.83
Ether (110°).....	14.66, 14.55
Volatile ether extract.....	(see below, volatile oil)
Alcoholic.....	27.6, 27.14

The proximate analyses were conducted in accordance with the usual methods¹ and gave the results tabulated below:

	Per cent.		Per cent.
Moisture.....	10.17	Protein.....	5.5, 5.3
Starch (diastase).....	7.7	Ash.....	6.5, 6.4
Pentosans.....	10.6	Dextrin.....	1.4
Crude fiber.....	17.15, 17.6		

A determination of the alcohol soluble carbohydrates was carried out by completely extracting 100 g. of the root with boiling neutral alcohol. The combined alcoholic extracts were concentrated under diminished pressure to a small volume, and enough water was added to completely precipitate the resin. This mixture was shaken repeatedly with ether in the volumetric flask, in order to remove as much of the resin as possible. The ether was removed with a pipet. The last traces of ether were removed by passing a current of air through the solution, which was thereupon precipitated with an excess of basic lead acetate solution and made up to a volume of 200 cc. This solution was filtered and the filtrate showed a rotation of -1.78° V, at 20° in a 2 dcm. tube. Lead was removed from the solution and 12.5 cc. were inverted by permitting it to stand in the presence of hydrochloric acid for 24 hours. The solution was neutralized and made up to a volume of 50 cc. This showed a rotation of -0.6° in a 2 dcm. tube. The percentage of sucrose calcu-

¹ U. S. Dept. Agr., Bur. of Chem., *Bull.* 107 (revised).

lated by Clerget's formula is 1.64%. It is further indicated that the reducing sugar is levulose in an amount of approximately 0.51%. Gravi-metric estimations of the sugars by the Munson and Walker modification of Fehling's process gave 1.87% sucrose and 1.0% of reducing sugar.

Sumbul root was examined for the presence of alkaloids by extracting a 200 g. sample with Prolius' solution but with negative results.

Volatile oil was determined, first by steam distilling one kilo of the coarsely ground drug for a few hours. The yield was 6.8 g. oil corresponding to 0.68%. When a 500 g. sample of finely sieved material was distilled for several days 5.51 g. of oil (1.1%) was obtained.

The oil on standing deposited a few yellow crystals that melted at 113-114° but these were not identified. The oil had a specific gravity of 0.932 at 15°. Upon distillation the higher fractions turned dark blue in color. A qualitative test for sulfur was negative.

B. Complete Examination of Alcoholic Extract.—For this purpose 56.7 kg. were exhausted by percolation with cold 95% alcohol. The percolate (327 l.) was concentrated under diminished pressure to a volume of 15.7 liters (1 l. = 3.6 kg. sumbul root).

Two liters of this extract were poured into 8 l. of distilled water and vigorously shaken. A heavy, sticky, viscous, light brown, semi-liquid separated. After standing 24 hours the aqueous layer was decanted, and the resin was washed with a second addition of distilled water. The resin weighed 1231 g. = 17.1%. A second 2 liter portion gave 1251 g. A third lot was precipitated and the resin fraction on the one hand, and the fraction representing the water-soluble constituents on the other, were studied separately.

The Examination of the Water-Soluble Constituents.—This solution (30 l.) contained the water-soluble constituents from 6 l. of the alcoholic extract representing 21.6 kg. of the root. It contained 520 g. of material and was concentrated to a volume of 3 l. under reduced pressure. The distillate obtained was distinctly acid. It was therefore rendered alkaline with barium hydroxide and concentrated to a small volume, again rendered acid and steam distilled. Acetic acid was identified as the silver salt.

Calc. for $C_2H_3O_2Ag$: Ag = 64.6. Found: 64.1%.

The concentrated solution was extracted repeatedly with large volumes of ether. The ethereal solution, which contained 46 g. of material, was concentrated to a small volume and fractionally extracted with solutions of hydrochloric acid (10%), water, ammonium carbonate, sodium carbonate, and potassium hydroxide successively. Nothing definite was isolated from these fractions, although the sodium carbonate fraction upon acidification yielded slight amounts of crystalline material.

The aqueous solution which had been completely extracted, was ex-

tracted with chloroform, which removed 13 g. of dark, oily material, from which nothing of a crystalline nature could be obtained. The aqueous layer, after the above-mentioned ether and chloroform extractions, was repeatedly shaken with hot amyl alcohol. The combined amyl alcoholic extracts were concentrated and washed repeatedly with water until free from reducing sugar. Upon further concentration of the amyl alcoholic extracts several crops of brown amorphous hygroscopic material separated. These could not be crystallized. The amyl alcohol was completely removed. Altogether 122 g. of material were present in this fraction, but its dark-colored, varnish-like nature prevented crystallization even after prolonged standing. For acid hydrolysis 42 g. were digested for two hours with 5% dilute alcoholic sulfuric acid. Upon removal of the alcohol, a smear separated. Water was added and the whole subjected to a steam distillation. The oily distillate which had an odor resembling furfuraldehyde failed to give the furfuraldehyde test. When the contents of the flask which had been steam-distilled had cooled a black resin separated, in which were admixed wart-like aggregates of crystalline material. The resin was therefore repeatedly extracted with boiling water. This was facilitated by blowing steam through the mixture. Altogether 2.9 g. of crystalline material separated from these watery extractions. The product was crystallized from dilute alcohol and from hot water. It separated in beautiful star-like aggregates of fine needles, melting at 227° . These crystals gave a blue fluorescence in alkaline solution. They were identified as umbelliferon.

Calc. for $C_8H_6O_3$: C, 66.67; H, 3.7. Found: C, 66.63; H, 3.9.

The black resin was dissolved in alcohol, poured upon purified sawdust and extracted with various solvents, but no crystalline compounds were isolated from it.

The combined acid aqueous liquid from which umbelliferon had crystallized, was concentrated to a small volume and extracted with ether, which dissolved a further quantity of umbelliferon. The sulfuric acid was quantitatively removed from the aqueous solution, from which *d*-phenyl glucosazone melting at $204-205^{\circ}$ was prepared. No pentose sugar was present. The quantity of reducing sugar present was equivalent to 11.27 g. glucose.

One of the products extracted by amyl alcohol is therefore distinctly shown to be glucosidic in nature, and is undoubtedly a body similar or isomeric with the glucoside of *Skimmia japonica*.¹

The aqueous liquid which had been extracted with ether and with amyl alcohol was freed from the latter immiscible solvent by means of a vigorous steam distillation. The total volume at this point was 10 liters.

The distribution of nitrogen in this solution was as follows: Total

¹ Eykman, *Receuil trav. chim. pays-bas.*, 1884, p. 204.

soluble nitrogen, 3.8 g. or 0.017%; ammonia nitrogen, 1.23 g. or 0.0057%; lead subacetate precipitable nitrogen, 1.31 g. or 0.0068%; nitrogen precipitated with phosphotungstic acid, 0.463 g. or 0.0021%.

In order to test for acid amides such as asparagine and glutamine, one-fifth of the solution was precipitated with mercuric acetate solution, but only a very slight separation took place. Its subsequent examinations for asparagine, glutamine, and allantoin were negative.

The remaining four-fifths was completely precipitated with basic lead acetate, whereupon a precipitate separated. This was removed by filtration and decomposed with hydrogen sulfide in the usual manner. The material precipitated with lead subacetate weighed but six grams. The usual tests for tannin were negative. It was mixed with purified sawdust and extracted with various solvents but this led to no pure products. An alkaline hydrolysis yielded no definite compounds.

The filtrate from the lead subacetate precipitate was freed from the excess of lead with hydrogen sulfide and after filtering off the lead sulfide, the filtrate was concentrated to a syrup. A small portion of this syrup, which has been shown to contain levulose and sucrose yielded a heavy crystalline deposit of pure *d*-phenylglucosazone which melted and decomposed at 210–211°. Pentose sugars were absent.

The remainder of this solution was precipitated with an excess of phosphotungstic acid in the presence of 5% sulfuric acid, and the resulting precipitate was removed by filtration, washed with 5% phosphotungstic acid wash and decomposed by the method of Wechsler.¹

The solution of the basic products was made up to a volume of 500 cc.

25 cc. distilled with MgO yielded no ammonia.

25 cc. required by the Kjeldahl method 12.58 cc. 0.1 *N* acid.

The remainder of the solution of basic products was concentrated to a syrup at 33°. This was extracted with 150 cc. of absolute alcohol and filtered. The alcohol was removed, and upon again treating the residue with absolute alcohol an amorphous hygroscopic solid separated. The filtrate from this now proved to be freely soluble in absolute alcohol and upon the addition of concentrated hydrochloric acid crystals consisting chiefly of betaine hydrochloride separated. The yield amounted to 0.5 g. or 0.019%. These crystals were not quite homogenous. After several crystallizations from alcohol the melting point was about 229–232°. Some parts of the crystalline mass which had the typical appearance of betaine hydrochloride could be picked out, and after rinsing with absolute alcohol the melting point found was 235°. The chlorine determination also indicated the presence of another base.

Calc. for $C_4H_{11}O_2N.HCl$: Cl, 23.1%. Found: Cl, 24.5%.

¹ *Z. physiol. Chem.*, 73, 138 (1911).

Pure betaine was identified after a fractional crystallization as the gold salt.

Calc. for $C_5H_{13}O_2N.AuCl_4$: Au, 43.1%. Found: Au, 43.2%.

Cholin was absent. A fractional crystallization of the mercuric chlorides failed to indicate any separations. The most insoluble fraction of the mercuri-chlorides when decomposed with hydrogen sulfide, and converted into the corresponding gold salt yielded a very pure sample of betaine aurichloride melting at $246-247^\circ$ and containing 43.1% gold. The melting point of the following fraction was $239-240^\circ$ and it contained 42.7% gold. The base here is chiefly betaine, but another substance is also present in the fraction.

The Examination of the Resin.—The resin precipitated when the alcoholic extract was poured into water weighed about 3.7 kg. This in alcoholic solution was poured upon purified sawdust, after it had been ascertained that nothing crystalline could be directly separated from it. A suitable quantity of the dried impregnated sawdust was transferred to a continuous extractor and extracted with the following results:

Petroleum ether ($40-60^\circ$).....	357 g.
Ether.....	316
Chloroform.....	46
Ethyl acetate.....	19
Alcohol.....	18
Total.....	756 g.

The Ligroin Extract.—This extract amounted to 357 g. It was dissolved in 2 liters of ether and then extracted with solutions of hydrochloric acid, water, and ammonium carbonate. None of these extractions yielded definite products. The ethereal solution was now shaken with a solution of potassium carbonate whereupon an emulsion formed. The mixture was acidified and then a clear ethereal solution was recovered which was successfully extracted with a ten per cent. solution of potassium hydroxide. The combined potassium hydroxide extractions were acidified and extracted with ether, and from this ethereal solution the substances soluble in aqueous potassium carbonate solution could now be extracted, leaving at length an ethereal solution containing 62 g. The constituents of the ether solution which were soluble in potassium carbonate solution were again extracted with ether after acidifying the solution of the potassium salts. The solution was dried over anhydrous sodium sulfate and the ether removed. The residue which weighed 32 g. was distilled under diminished pressure. The boiling point was $234-275^\circ$ at 28 mm. and it had an iodine number of 101.3. These fatty acids were studied in connection with those obtained upon the subsequent hydrolysis of the glycerides.

The material soluble in potassium hydroxide solution was almost

entirely removed from its ether solution by fractional extraction with one per cent. potassium hydroxide solution. Upon acidification this resin could be obtained as a brittle solid. It yielded the same products when hydrolyzed in acid and in alkaline alcoholic solution. The acid hydrolysis, however, was more satisfactory, and after heating for many hours with 5% alcoholic sulfuric acid the alcohol was removed by steam distillation.

The steam distillate yielded a small quantity of an oil resembling the volatile oil of sumbul. The fraction boiling below 230° was colorless while the fraction boiling at $230-250^{\circ}$ was dark blue in color.

The black resinous hydrolysis products, contained in the flask were extracted with ether. The ether was extracted with solutions of ammonium carbonate, potassium carbonate, and potassium hydroxide. From the ammonium carbonate extract, vanillic acid was obtained. It melted at 206.5 to 207.5° . It was dried at 125° and analyzed.

Calc. for $C_8H_8O_4$: C, 57.1; H, 4.8. Found: C, 57.1; H, 4.7.

The methyl ester, prepared in the usual manner, melted at $62-63^{\circ}$.

The potassium carbonate extraction showed a blue fluorescence, but nothing could be obtained from it. The potassium hydroxide solution removed most of the hydrolytic products. These were recovered and again hydrolyzed with a further quantity of 5% alcoholic sulfuric acid, but no further yield of vanillic acid was obtained. The material soluble in potassium hydroxide solution was fractionally distilled at a pressure of 17 mm. Five fractions were obtained: (I) up to 150° , (II) $150-170^{\circ}$, (III) $170-205^{\circ}$, (IV) $205-212^{\circ}$, (V) above 212° . Fractions I, II, III were solids from which a considerable quantity of vanillic acid ($206-207^{\circ}$) was isolated. The upper fractions were amber-colored oils that solidified. They resemble somewhat the higher boiling fractions obtained in the unsaponifiable fraction of the fat.

The original ethereal solution which had been extracted as described above was evaporated to dryness and the residue of neutral substances was saponified by boiling with 700 cc. of ten per cent. alcoholic potash for about seven hours. The alcohol was removed and water added in sufficient quantity to completely precipitate the unsaponifiable material. This was extracted with ether.

Examination of the Unsaponifiable Matter.—The dried solution was evaporated to dryness and the residue proved to be an oil which could not be directly crystallized. The material was divided into two equal parts and fractionally distilled under diminished pressure. The results upon the first half were as follows:

Fraction I. (B. p. $100-174^{\circ}$ at 27–24 mm.) This was a yellowish limpid oil with a somewhat fragrant odor and amounted to about 7 g.

Fraction II. (B. p. $174-190^{\circ}$ at 25 mm.) This is an olive-green

oil amounting to about 11 g. The viscosity seemed to increase noticeably and the fraction was therefore stopped at 190°.

Fraction III. (B. p. 190–205° at 28 mm.) This was a thick olive-green oil amounting to about 14 g.

Fraction IV. (Up to 267° at 30 mm.) This is a thick viscid fraction which did not solidify and weighed about 23 g.

Fraction V. (B. p. 290–360° at 17 mm.) This weighed 4.4 g. and partially solidified.

The other half of the unsaponifiable material was distilled in approximately the same manner and the light, limpid fragrant oils which constitute the lower boiling fractions were fractionally distilled several times.

The fractions were as follows:

Fraction I. (Up to 140° at 15 mm.) This fraction had no sharp boiling point as some of the material boiled at 80°. It is a very mobile yellow oil.

0.1807 g. absorbed 0.301 g. iodine; iodine number, 166.6. 0.1902 g. subst. gave 0.1815 g. H₂O and 0.5564 g. CO₂. Found: C = 79.8; H = 10.7.

Fraction II. (B. p. 140–170° at 18 mm.) This is a yellow oil, slightly less mobile than Fraction I. It was rather fragrant and was unsaturated.

Fraction III. (B. p. 175–180° at 15 mm.) This fraction appeared to possess an almost constant boiling point. It was redistilled and most of it passed over at 168–173° at 12 mm. It was light green in color and not more than slightly mobile unless warmed. The specific gravity at 15° was 1.0052 and $[\alpha]_D^{26}$ was -17.41° .

2.3353 g. made up to 20 cc. with chloroform showed a rotation of -4.06° in a 2 dcm. tube

0.1393 g. subst. absorbed 0.2432 g. iodine; iodine number, 174.6. 0.1982 g. subst. gave 0.1482 g. H₂O and 0.5596 g. CO₂. Calc. for C₂₇H₄₆O: C = 76.75; H = 10.5. Found: C = 77.0; H = 10.4.

The other fractions boiling above 180° and below 270° were thick viscid oils and seemed similar to the material which usually accompanies the phytosterols in this fraction, but the amount present in sumbul root is unusually large. It amounted to about one-half of the entire fraction.

The highest boiling fraction yielded, when crystallized from ethyl-acetate, 2.0 g. of a phytosterol melting at 134–135°.

Calc. for C₂₇H₄₆O.H₂O: H₂O = 4.5. Found: 4.97.

Calc. for C₂₇H₄₆O: C = 83.9; H = 11.9. Found: C = 84.0; H = 12.1.

0.4786 g. anhydrous material made up to 20 cc. with chloroform showed a rotation of 1.42° in a 2 dcm. tube, whence $[\alpha]_D^{20} = -29.7^\circ$.

It yielded an acetyl derivative, that separated from acetic anhydride in thin, elongated plates terminating in an angle at one end, and melting at 121–122°. When recrystallized from ethyl acetate the melting point was unchanged. The filtrate from which this 2 g. of phytosterol separated

yielded upon concentration 1.3 g. further. Recrystallized once it melted at $133-134^{\circ}$ and yielded an acetate identical in appearance with the one just described. The melting point of the acetate separating from acetic anhydride was $118-120^{\circ}$ which was elevated to $120-121^{\circ}$ by one recrystallization.

Examination of the Volatile Fatty Acids.—The alkaline solution from which the unsaponifiable matter had been extracted with ether was divided into two equal parts, each of which, after acidification with dilute sulfuric acid, was steam distilled for eight hours. The odor of the distillate resembles that of infusion of hops. The combined distillate was almost neutralized with 656 cc. of 0.41 *N*, barium hydroxide solution. This was concentrated under diminished pressure to a volume of 200 cc. and acidified with hydrochloric acid, whereupon a quantity of oil separated which was extracted with ether. The solution was dried over anhydrous sodium sulfate and the ether removed. The residue, weighing about 17 g. was fractionally distilled at atmospheric pressure. The distillate was caught in three fractions: (I) up to 157° ; (II) $157-190^{\circ}$ (6.2 g.); (III) $190-200^{\circ}$ (9.5 g.). The third fraction, when allowed to stand in the ice chest, yielded a crop of beautiful crystals of tiglic acid melting at 61° . The fractions above recorded were now subjected to a systematic fractional distillation and five fractions were obtained.

Fraction I. (B. p. up to 125° .) This fraction was neutralized with ammonium hydroxide, concentrated in order to remove the excess of ammonia and treated with silver nitrate solution. It contained a small quantity of acetic acid as was shown by the analysis of the silver salt that separated.

0.1171 g. gave 0.0717 g. silver. Calc. for $C_2H_3O_2Ag$: Ag = 64.6%. Found: 61.2%.

Fraction II. (B. p. $125-165^{\circ}$.) This was an intermediate fraction, amounting to about 3 g. It had the odor of acetic acid combined with that of valerianic or butyric acid.

0.1331 g. gave 0.1030 g. H_2O and 0.2377 g. CO_2 . Found: C = 48.7; H = 8.85.

Calc. for $C_2H_3O_2$: C = 40.0; H = 6.7%; for $C_4H_7O_2$: C = 54.5; H = 9.1%; for $C_6H_{11}O_2$: C = 58.8; H = 9.8%; for $C_4H_9O_2$: C = 60.0; H = 8.0%.

The analytical data indicates a mixture of butyric and acetic acids.

Fraction III. (B. p. $165-180^{\circ}$.) This fraction had the odor of butyric and valerianic acids. When dissolved in aqueous solution of sodium carbonate it instantly reduced potassium permanganate solution in the cold and it therefore contained a quantity of unsaturated acid.

0.2152 g. gave 0.1549 g. H_2O , and 0.4308 g. CO_2 . C = 54.6; H = 8.1.

This fraction consists essentially of butyric and angelic acids.

Fraction IV. (B. p. $180-190^{\circ}$.) C = 59.7; H = 8.33. This fraction was converted into the silver salts which had a constant composition

Calc. for $C_4H_7O_2Ag$: Ag = 55.4; for $C_5H_9O_2Ag$: Ag = 51.7; for $C_6H_7O_2Ag$: Ag = 52.2. Found: I, Ag = 52.1; II, Ag = 52.0.

Fraction V. (B. p. 190–195°) C = 59.8; H = 8.1.

These fractions are mixtures of angelic and tiglic acids. The solid acid which was repeatedly separated by freezing the high boiling fraction, melted at 62–63°, and when analyzed gave results agreeing with those required by tiglic acid.

Calc. for $C_5H_9O_2$: C = 60.0; H = 8.0. Found: C = 60.1, H = 8.1.

The aqueous liquid from which the above-described acids had been extracted with ether was again steam distilled and yielded a crop of crystals of almost pure silver acetate.

Calc. for $C_2H_3O_2Ag$: Ag = 64.6. Found: Ag = 64.1%.

Examination of the Nonvolatile Fatty Acids.—The acid mixture which had been steam distilled for the removal of the fatty acids was cooled and extracted with ether. From the dried solution the ether was removed and the residue digested with a large volume of low boiling petroleum ether. A considerable quantity of a sticky, brown smear proved to be insoluble. The petroleum ether was removed and the fatty acids distilled. They had an iodine number of 121, and boiled chiefly at 230–260° at 15 mm. However, a considerable quantity came over at lower temperatures, showing that the steam distillation had not completely removed the lower acids. The first distillate crystallized upon cooling and proved to be tiglic acid melting at 63–64°. Furthermore a fraction boiling above 260° was caught. The weight of these acids was 19.2 g.

This was mixed with the acids which had been originally extracted with potassium carbonate solution. Of this mixture a portion weighing 22.4 g. was separated into the solid and liquid acids. The latter weighed 16 g., thus constituting about 71% of the fatty acids. These boiled chiefly at 215–245° at 15 mm., although they seemed to contain a trace of the lower acids.

Calc. for $C_{18}H_{34}O_2$: C = 76.6; H = 12.1; iodine no. = 90.1; for $C_{18}H_{32}O_2$: C = 77.1; H = 11.4; iodine no. = 181.4; for $C_{18}H_{30}O_2$: C = 77.7; H = 10.8; iodine no. = 274.0. Found: C = 77.3; H = 11.2; iodine no. = 138.7, 138.7.

The liquid acids therefore consist of oleic and linoleic acids with perhaps a small quantity of linoleic acid.

The solid acids weighed 4.1 g. A quantity of cerotic acid equivalent to 33% of the solid acids was obtained. It melted at 74–75°.

Calc. for $C_{26}H_{50}O_2$: C = 78.8; H = 13.1; N. V. = 141.7. Found: C = 78.4; H = 13.0. N. V. = 140.7.

The alcoholic filtrate from the cerotic acid yielded a quantity of a mixture of palmitic and stearic acids melting at 52–53°.

Calc. for $C_{16}H_{32}O_2$: C = 75.0; H = 12.5; N. V. = 219.1; for $C_{17}H_{34}O_2$: C = 76.1; H = 12.7; N. V. = 197.5. Found: C = 75.6; H = 12.5; N. V. = 205.3.

The Ether Extract of the Resin, which amounted to 316 g., was obtained in two extractions of the sawdust which had been impregnated with the resin, as above described. The first extract amounting to 300 g. was very soluble, while the second ether extract (16 g.) was obtained by prolonged extraction and upon standing tended to separate as a tar.

The first extract was concentrated and after prolonged standing a small quantity of a white micro-crystalline product separated. When this substance was dissolved in chloroform, in the presence of a few drops of acetic anhydride, and sulfuric acid was added a play of colors resulted showing at first transient pink, then blue, and finally a beautiful green. It melted at $260-270^{\circ}$, and after crystallization from dilute pyridine it melted at about 290° . It was a phytosterolin.

Calc. for $C_{28}H_{48}O_2$: C = 72.3; H = 10.2. Found: C = 72.6; H = 10.2.

A small portion was converted into an acetate, which crystallized from a mixture of dilute alcohol and ethyl acetate in beautiful plates, melted at $159-160^{\circ}$.

A portion of the ethereal filtrate from the above-mentioned phytosterolin was shaken with a 30% sodium bisulfite solution. The aqueous solution was drawn off, acidified with H_2SO_4 and allowed to stand until the sulfur dioxide had been dissipated. The solution now had an aromatic fragrance. It was extracted with ether. The ether solution showed a residue of an insignificant amount of oil. This was subjected to the color tests characteristic for vanillin. With ferric chloride a green color resulted, similar to the color resulting with dilute vanillin solutions. The phloroglucin and hydrochloric acid test showed a light pink coloration. It is therefore quite probable that this resin contains a trace of vanillin.

A quantity of this resin (277 g.) was dissolved in ether and extracted successively with water, and with solutions of ammonium carbonate, potassium carbonate, and potassium hydroxide. The ether was then washed with water and the solvent removed. This *neutral constituent* weighed 116 g. or 42% of the ether extract. It is an extremely sticky substance and when warmed can be pulled into shiny, silken-like threads. It is very soluble in alcohol. In order to find out whether it was ester like corresponding to the "resinotannolester" group of Tschirch, or a stable substance incapable of hydrolysis ("resene") estimations were carried out upon its saponification value.

1.898 g. boiled 0.5 hr. with 23 cc. 0.5 *N* KOH (alcoholic), neutralized 0.3136 g. KOH. S. V. = 165.

1.898 g. boiled 1.0 hr. neutralized 0.333 g. KOH. S. V. = 175.5.

1.898 g. boiled 5 hrs. neutralized 0.3416 g. KOH. S. V. = 179.

It appeared, therefore, that some insight into the composition of this amorphous resin might be gained by hydrolysis. For this purpose 35.5 g. were dissolved as far as possible in 350 cc. of 10% KOH, and steam

was passed through the mixture for about one week. The liquid when acidified gave an oily precipitate, and the acid filtrate was examined for organic acids with negative results. Saponification with 20% KOH solution for a somewhat longer period gave no smooth reaction, although small quantities of volatile acids were detected as decomposition products.

Another portion (33 g.) was hydrolyzed by the method of Tschirch¹ using at first sulfuric acid 1 : 2. After distilling with steam for 4 days, 0.915 g. of umbelliferon was obtained. The strength of the sulfuric acid was increased to 1 : 1 and after about ten days 3.86 g. further of umbelliferon was obtained. The total umbelliferon corresponds to 14.3% of the neutral portion. It gave the characteristic fluorescence with alkalis, and after recrystallizations from water, dilute alcohol, and ethyl acetate melted at 228°.

Calc. for $C_9H_6O_3$: C = 66.67, H = 3.7. Found: C = 66.86, H = 3.43.

The resin or ester is therefore somewhat similar to some other resins of the umbelliferae such as galbanum, sagapen, asafoetida, which yield umbelliferon when thus hydrolyzed.

The ammonium carbonate extract of the ether extract of the resin was acidified and permitted to stand for some time when a quantity of tar separated. This was removed by filtration and the clear aqueous acid filtrate thoroughly extracted with ether. This solution was evaporated to dryness and dried *in vacuo* over sulfuric acid. When now it was digested with small volumes of anhydrous ether a white crystalline deposit remained, weighing 0.24 g. It was crystallized from water whereupon it melted at 205–206°. It was dried for 2.5 hours at 125° and analyzed. The remainder was again recrystallized from dilute alcohol whereupon it separated in needles and the melting point remained constant. This was dried at 115° and also analyzed.

I. 0.0853 g. subst. gave 0.1802 g. CO_2 and 0.0357 g. H_2O . II. 0.0641 g. subst. gave 0.1351 g. CO_2 and 0.0270 g. H_2O .

Calc. for $C_9H_6O_4$: C = 57.1; H = 4.8. Found: C = 57.61, 57.48; H = 4.69, 4.73.

This acid appears to be vanillic acid (3-methoxy protocatechuic acid). This was further substantiated by the determination of the methoxyl group upon another small sample.

The potassium carbonate extract of the ether extract upon acidification yielded a tar which was removed by filtration. From the filtrate about 0.2 g. of umbelliferon was isolated. Recrystallized from hot water it melted at 226° and when a mixture of this product with the umbelliferon that was obtained from the glucoside by hydrolysis was melted, the melting point was 227°.

Calc. for $C_9H_6O_3$: C = 66.67; H = 3.7. Found: C = 66.9; H = 3.7.

¹ "Die Harze und die Harzbehälter," 1906, p. 342.

When the potassium hydroxide extract was redissolved in alcohol it was impossible to obtain crystalline products even after the solution was stood aside for months. Thus the resinous extract weighed 143 g., equivalent to 52% of the ether extract. It showed no ester properties, and was in fact a resin acid. (Acid no. = 129.) A portion (106 g.) was dissolved in a large volume of ether and again extracted with solutions of ammonium carbonate and of potassium carbonate. The ammonium carbonate solution was acidified and a smear precipitated, indicating that the substances extracted with potassium hydroxide had undergone change. The filtrate from this smear yielded a quantity (0.1 g.) of vanillic acid that melted after recrystallization from water at 204–205°. A methoxyl determination was carried out upon this, by the Zeisel method as modified by Perkin.

Calc. for $C_8H_8O_4$: OCH_3 = 18.4%. Found: 18.3%.

The potassium carbonate extract contained a small quantity of umbelliferon.

The potassium hydroxide extractions were made with successive portions of 100 cc. of a one per cent. solution. These were each washed once with ether and then acidified with hydrochloric acid and the sumbul resin acid was again extracted with ether. The ether was removed and the residues were dried in a vacuum over sulfuric acid. The first four extracts weighed about 12 g. each and the fifth to the tenth and last extract were smaller. Fourteen grams of material could not be extracted with 1% potassium hydroxide solution. The fractions of this resin acid were examined and found to be mixtures, although they were all similar light-colored powders when dry and of a hygroscopic nature. When very slightly moistened with alcohol they became exceedingly sticky and resinous.

Fraction III. This was a typical product. It softened at 56–60° and became translucent at 63°, and decomposed with effervescence at 75–85°. It was analyzed: C = 72.3%; H = 8.1%. It had an acid number of 118–122, and was optically active.

0.474 g. made up to 50 cc. with 95% alcohol showed a rotation of -1.18° in a 2 dcm. tube, whence $[\alpha]_D^{21.5} = -62.2^\circ$.

Fraction IV. This fraction softened at 50° and was completely translucent at 53°. It effervesced at about 80–90°. Analysis showed: C = 73.3%; H = 8.2%; acid number = 123.

0.3942 g. made up to 20 cc. with 95% alcohol showed a rotation of 2.22° in a 2 dcm. tube, whence $[\alpha]_D^{19.5} = -56.3^\circ$.

Fractions V and VI. The optical rotation was taken.

V. 0.4293 g. made up to 20 cc. with 95% alcohol showed a rotation of 1.98° in a 2 dcm. tube, whence $[\alpha]_D^{20} = -46.0^\circ$.

VI. 0.7665 g. made up to 20 cc. with 95% alcohol showed a rotation of 1.56° in a 1 dcm. tube, whence $[\alpha]_D^{22} = -40.6^\circ$.

It is therefore obvious that this sticky acid of a resinous nature, which forms a most conspicuous part of sumbul extract and gives the latter its disagreeable properties is not a homogenous body. The presence of vanillic acid in the solution after prolonged standing of the alcohol solution suggested that this phenolic acid represents a part of the structure of the complex resin and a methoxyl determination of the resin acid further indicates this.

Subst. 0.1918 g.: $\text{CH}_2\text{I} = 0.0641$. Found: $\text{OCH}_3 = 4.4\%$.

Vanillic acid was prepared from this resin acid as follows: thirteen grams were boiled for several hours with 5% alcoholic sulfuric acid. The alcohol was removed by steam distillation. The steam distillate contained a small amount of a blue oil resembling the essential oil.

The contents of the flask were shaken with ether, which was then extracted with solutions of ammonium carbonate, potassium carbonate, and potassium hydroxide. From the first of these extracts vanillic acid melting at $205-206^\circ$ was isolated: The weight was 0.5 g. The potassium carbonate extract yielded umbelliferon (0.05 g.) melting at $225-227^\circ$. Nothing definite could be isolated from the potassium hydroxide solution.

The chloroform extract of the resin (46 g.) was divided into two parts. The first (26 g.) was redissolved in chloroform and extracted with the various alkaline solutions but nothing definite could be separated by this process. Most of the material was extracted with potassium hydroxide solution. Twenty grams were hydrolyzed with 5% alcoholic sulfuric acid. Umbelliferon (0.85 g.) melting at $226-227^\circ$ was isolated. This was present in glucosidic combination, as 1.5 g. of *d*-phenyl glucosazone melting at $206-207^\circ$ was isolated.

The ethyl acetate extract of the resin (19 g.) was a dark-colored resinous product. Upon hydrolysis a small amount of umbelliferon melting at $226-227^\circ$ was isolated, but sugar was not formed. The material is therefore not glucosidic.

The alcohol extract of the resin (18 g.) agreed in its properties with the brown glucosidic powder isolated from the amyl alcohol extract of the constituents soluble in water. Umbelliferon and a reducing sugar were found as products of an acid hydrolysis.

KALAMAZOO, MICH.

[CONTRIBUTION FROM THE LABORATORY OF THE DODGE AND OLCOTT Co.]
SOME DERIVATIVES OF COUMARIN.¹

By FRANCIS D. DODGE.

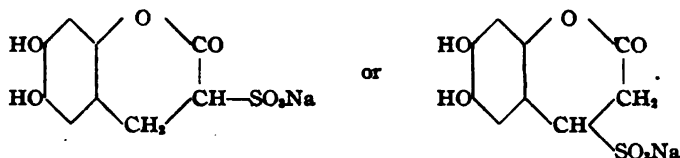
Received November 22, 1915.

The behavior of unsaturated lactones, or more particularly, the coumarins, with the alkaline bisulfites, appears so far to have been studied in but one instance.

¹ Presented at the meeting at New Orleans, Mar., 1915.

Rochleder,¹ in 1863, described a compound derived from aesculetin, to which he gave the formula $C_9H_6O_4 \cdot NaHSO_3 \cdot \frac{1}{2}H_2O$. From this a beautifully fluorescent substance termed "aescorkein" was obtained, which was further studied by Liebermann.²

The latter showed that the compound of Rochleder's was not an ordinary addition product, like the aldehyde compounds, but was in reality a sulfonic derivative of hydro-aesculetin.



The free sulfonic acid was obtained in crystalline form, easily soluble in water and alcohol, having the composition $C_9H_6O_7S \cdot H_2O$. At 95° , it decomposes smoothly into aesculetin and sulfurous anhydride. By treatment of the sodium sulfonate with acetic anhydride and sodium acetate, a similar reaction occurred, yielding diacetyl aesculetin. Liebermann further states that no analogous derivatives could be obtained from umbelliferon, daphnetin, diethyl aesculetin, or tri-ethyl aesculetinic acid.

The writer has observed, however, that coumarin and limettin (a dimethoxy-coumarin) readily yield well defined and beautifully crystalline sulfonic compounds, which, in several reactions, exhibit a rather interesting behavior.

Sodium Hydrocoumarinsulfonate.—If coumarin is warmed with six parts of a 20% sodium bisulfite solution, on the water bath, with frequent shaking, for fifteen minutes to one-half hour, it dissolves completely, and, on cooling, the liquid solidifies to a mass of crystals, which, after filtering and washing with cold water, are nearly pure. Recrystallization from water effects a further purification, but is accompanied with much loss, owing to the solubility of the compound. From the mother-liquors a further yield is obtained by "salting out" with common salt, and recrystallization.

Calc. for $C_9H_6O_7 \cdot NaHSO_3 \cdot H_2O$: H_2O , 6.72%; Na_2SO_4 , 26.45%. Found: H_2O at 100° , 6.43; Na_2SO_4 (ignition H_2SO_4), 26.14.

Titration: (1) 1.25 g. required 9.3 cc. 0.5 N KOH (calc. 9.15 cc.); (2) 2.1015 g., 15.3 cc. (calc. 15.38 cc.); (3) 10.00 g., 73.6 cc. (calc. 73.2 cc.).

As already stated, the compound is quite soluble in water, a saturated solution at 15° containing about 20% of hydrated salt.

The reaction of the aqueous solution is neutral, but if alkali be added, an immediate reaction occurs, and, as shown above, the compound may

¹ *Wien. Akad. Ber.*, 55, 819; *J. prakt. Chem.*, 101, 415.

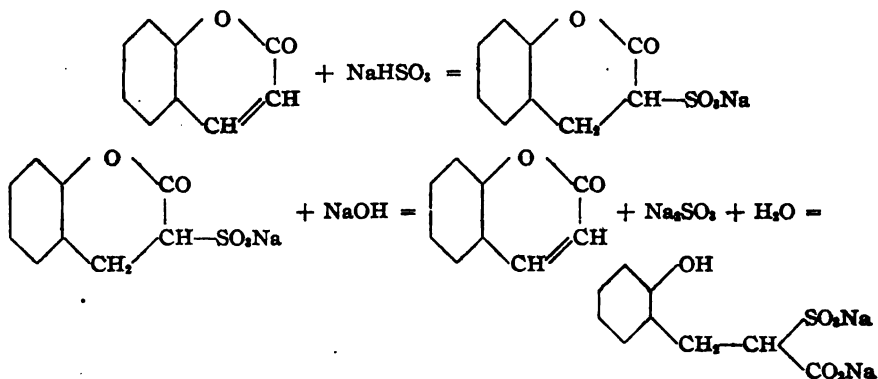
² *Ber.*, 13, 1595 (1880); 14, 477 (1881); 34, 2608 (1901); 35, 2919 (1902).

be titrated with accuracy, giving results which indicate the absorption of one molecule of alkaline hydroxide.

With a concentrated solution of the compound, the addition of a small amount of 0.5 *N* hydroxide causes an immediate turbidity, which soon becomes a crystalline precipitate of coumarin. On continued agitation, the crystals redissolve and the solution becomes neutral, and further addition of alkali causes a repetition of the phenomena. If the alkali is added quickly, in larger amount, a crystalline magma results which slowly dissolves. Finally, coumarin ceases to separate, and the liquid becomes permanently neutral.

This solution does not contain the original compound, for no precipitate is obtained by saturating it with salt; nor has the sulfonic group been split off, since the iodine absorption is negligible. If, however, the coumarin which is formed by the quick addition of alkali is immediately filtered off, the filtrate shows the presence of much sulfite.

These phenomena have a plausible explanation if we assume the following reactions:



The crystalline sulfonate is, then, a derivative of hydrocoumarin, containing the lactone ring intact. Alkali splits off the sulfo group, liberating coumarin, which then recombines with the neutral sulfite, forming the open-chain hydrocoumaric acid derivative. The position of the sulfo group, whether α or β , remains to be determined. Coumarin, hence, should be soluble in neutral sulfite solution, which, in fact, is the case.

10 g. coumarin and 100 cc. of 25% sodium sulfite solution were allowed to stand at the ordinary temperature, with occasional shaking. After three days, the crystals were almost entirely dissolved, and the still neutral solution behaved in all respects like that obtained by titrating the hydrosulfonate. At 100° , the reaction is quicker, requiring about one-half hour.

Potassium Hydrocoumarinsulfonate.—This salt is readily prepared by warming coumarin with seven parts of 20% potassium bisulfite solution. On cooling, a mass of white needles is formed, which may be recrystallized from hot water. It is less soluble than the sodium salt, the saturated solution at 15° containing 7.6%.

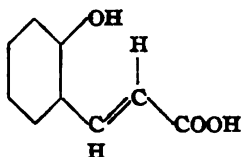
Calc. for $C_9H_6O_3 \cdot KHSO_3 \cdot H_2O$: H_2O , 6.33%. Found: 6.29.
2.0035 g. required 14.2 cc. 0.5 *N* KOH (calc. 14.1 cc.).

In other properties, it resembles the sodium salt.

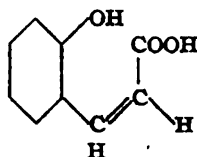
Other Salts.—The barium salt separates as a crystalline precipitate when a solution of barium acetate is added to a strong solution of the sodium salt. It is soluble in about 44 parts of water at 20°.

The copper salt is obtained in pale blue prisms, by slow concentration of the mixed solutions of sodium salt and copper sulfate.

Hydrocoumaric Acid Derivatives.—As is well known, coumaric acid, or *o*-hydroxycinnamic acid is supposed to exist in two stereoisomeric configurations.



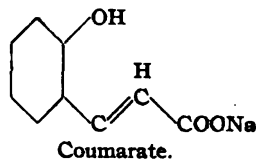
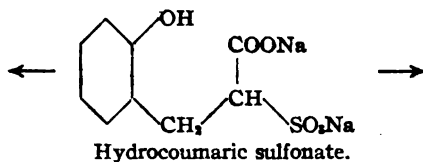
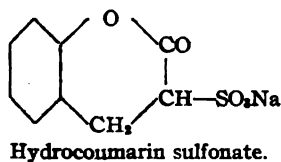
1. Coumaric acid.



2. Coumarinic acid.

The first, and only stable form, does not readily yield the lactone, coumarin, except indirectly, as, for example, by distillation of the acetyl derivative. In the second case, the proximity of the hydroxyl groups so favors the lactone formation, that the acid itself cannot be isolated; it is assumed to be present in the compounds obtained from coumarin by the action of alkalis at low temperatures.

Now, in the case of the hydrocoumaric sulfonate, with the disappearance of the double linkage, vanishes also the possibility of this kind of stereoisomerism. The hydrocoumaric derivatives are, in a sense, intermediate between the coumaric acids, and, by suitable reactions, it should be possible to pass at will to either the coumaric or coumarinic series.



This, in fact, is the case; by splitting off the sulfo group, coumaric acid results, while, by a simple dehydration, the lactone ring is re-established, giving the original hydrocoumarin sulfonate as shown on preceding page.

The solution of sodium hydro-coumaric sulfonate shows little tendency to crystallize. When highly concentrated, a viscid liquid is obtained, which in the desiccator solidifies to an indistinctly crystalline mass, which has not yet been purified. The barium salt, prepared by double decomposition, forms white needles, not very soluble in water.

Formation of Coumaric Acid.—2 g. hydrocoumarin sodium sulfonate were titrated with 0.5 *N* KOH, requiring 14.7 cc., or one molecule. A further addition of 14.7 cc. KOH, or one molecule, was then made, and the solution evaporated to small bulk. The residue was dissolved in 10 cc. water, and the solution titrated with 0.5 *N* HCl, of which 14.6 cc. were required. One molecule of alkali, hence, does not remove the sulfo group, under these conditions. The solution was again concentrated to 10 cc., 29.4 cc. 0.5 *N* KOH (2 mol.) added, and again evaporated, the solution now showing the yellowish green tint characteristic of the coumarates. On titration, 19 cc. 0.5 *N* HCl were required, showing a conversion of about 70%. On addition of concentrated hydrochloric acid to the filtered solution, the coumaric acid was precipitated nearly white, and was identified by the melting point and other properties of that acid. With larger excess of alkali, the yield appears to be almost quantitative.

This smooth reaction offers a convenient method for the preparation of coumaric acid, as the usual process, with sodium ethylate or very strong hydroxide, is somewhat troublesome. For example:

10 g. coumarin are heated with 100 cc. of 25% sodium sulfite until completely dissolved, and the liquid evaporated to about 50 g. 40 g. of 50% potassium hydroxide solution are now added, and the mixture evaporated to dryness on the water bath. The yellowish green residue is then dissolved in water, and the cooled solution acidified with strong hydrochloric acid. The precipitated coumaric acid is filtered and washed with cold water, and after drying, can be conveniently recrystallized from acetone. The yield is about 10 g.

Formation of Coumarin.—The hydrocoumaric sulfonate solution from 2 g. coumarin was evaporated to dryness, pulverized, and mixed with 5 cc. of acetic anhydride. On standing, the mixture becomes thick, and finally solidifies. After two days, the mass was broken up, filtered, and the adhering anhydride allowed to evaporate. The product was soluble in water, but, on adding alcohol, was precipitated in crystals. By recrystallization from water, hydrocoumarin sulfonate was obtained in the usual form.

Or, starting with coumaric acid, the reaction can be carried out in a similar manner.

2 g. coumaric acid were heated with 10 cc. of 30% sodium bisulfite several hours on the water bath, until a cooled sample gave no precipitate of acid on the addition of hydrochloric acid. The liquid was then evaporated to dryness, and the product pulverized. On treatment with acetic anhydride, the same behavior was observed, as with the product from coumarin. The yield of hydrocoumarin sulfonate, crystallized from water, was 1.75 g.

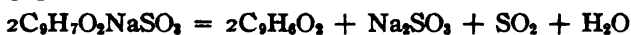
We have, then, here a cycle of reactions by which to pass from coumarin to coumaric acid, or *vice versa*.



The quantitative recovery of coumarin from the hydrosulfonate presents some difficulty, owing to the rapidity with which it is attacked by the neutral sulfite. Working quickly with ice-cold solutions, the yield is only about 30% of the theoretical; decomposition with barium hydroxide gave a little better result, the yield reaching 40%.

The hydrocoumarin sulfonate is also decomposed by alkaline carbonates, at ordinary temperatures—an exceptional reaction for sulfonic derivatives. On adding strong sodium carbonate solution to a 20% solution of the sodium salt, the mixture remains for a short time clear, then becomes turbid, and a little later the liquid is filled with a net-work of fine coumarin crystals. After a few hours, however, the crystals have entirely disappeared.

The regeneration of coumarin from the hydrosulfonate appears to be quantitative when the latter is heated at 130–160°, the following reaction taking place:



The evolution of sulfurous anhydride begins at about 120°, and the reaction is complete after two hours' heating at 150–160°. From the residual mixture of coumarin and sodium sulfite, the former is easily isolated by extraction with ether.

Limettin Derivative.—Limettin, also known as "citraptene," is a dimethoxycoumarin, $\text{C}_{11}\text{H}_{10}\text{O}_4$, easily obtained from the sediment which is deposited from the expressed oil of limes. By crystallization from acetone, it is deposited in yellow needles, melting at 148° (uncorr.). It can also be purified as follows:

10 g. crude limettin are shaken with 100 g. 5% sodium hydroxide solution, until no more dissolves. This may require some days. After filtering from dark resinous matter, 12 g. sodium bicarbonate are added. On standing, limettin gradually separates in yellowish white crystals, the yield from the crude being about 75%. Repetition of the process gives a still lighter colored product. A pure white preparation may be obtained from the hydrosulfonate, as described below.

Hydrolimettin Sodium Sulfonate.—With bisulfite solution, limettin does not react as readily as coumarin. At 100° , solution takes place very slowly, and a higher temperature was found more convenient.

10 g. limettin and 80 g. 20% sodium bisulfite solution were boiled gently one-half hour, till all was dissolved, except a little resin. The liquid was filtered while warm, and allowed to crystallize, finally at a low temperature. The resulting yellow crystals (7.5 g.), were recrystallized from two parts hot water. The sulfonate is thus obtained in fine, large plates, having the composition $C_{11}H_{10}O_4 \cdot NaHSO_3 \cdot 4H_2O$.

(1) 4.8365 g. air dry, lost at 100° , 18.65% (calc. 18.84%).

(2) 1.5355 g. dried, required 9.7 cc. 0.5 *N* KOH (calc. 9.9 cc.).

The salt is soluble in 6 parts water at 20° , and is precipitated on addition of common salt. On titrating the solution with 0.5 *N* alkali, limettin is immediately thrown out, and redissolves much more slowly than is the case with coumarin, owing no doubt to the very slight solubility of limettin in water. Attempts to prepare the limettic acid, corresponding to coumaric acid, were unsuccessful. An acid product was obtained, but it could not be crystallized. Limettin dissolves slowly in a 25% solution of sodium sulfite at 100° ; the solution is not precipitated by salt, nor does it yield crystals when concentrated.

Hydrolysis of Coumarin.

The phenomena observed when one attempts to hydrolyze coumarin quantitatively in the usual manner with alkaline hydroxides, are peculiar and of some interest. In fact, the uncertain results frequently encountered in the titration of lactones have already been noted by Baeyer,¹ and are not surprising, when one considers that the tendency to lactone formation is opposed to the hydrolysis, and a condition of equilibrium between lactone and alkaline salt is to be expected.

If coumarin, in alcoholic solution, is titrated at the ordinary temperature with 0.5 *N* alkali, the neutralization is found to be very slow. For example: 2.053 g. coumarin were dissolved in 10 cc. alcohol, and 0.5 *N* alcoholic potassium hydroxide added slowly at intervals, keeping the solution just alkaline to phenolphthalein. After 24 hours, 1.6 cc. had been used, indicating 5.6% coumarin converted into salt.

With excess of alkali, the conditions are different; the hydrolysis appears to be complete; and the titration can be made with approximate accuracy. But as soon as the excess of alkali is neutralized, formation of coumarin begins and continues until the point of equilibrium is reached, the solution becoming alkaline. If, now, the free alkali be again neutralized, a further production of coumarin is observed, and so on until a permanent equilibrium between the coumarin and the salts present is attained, which point depends, of course, on the concentration, temperature, etc.

¹ *Ber.*, 30, 1956 (1897).

If, at this point, the free coumarin be removed, as for example, by extraction with ether, the equilibrium is again disturbed, and a further liberation of coumarin occurs.

A remarkable feature of the reaction is the slowness with which it progresses, and it would seem that a careful study, by physico-chemical methods, would not be without interest.

In the examples given below, it will be noticed that the results of the first titration are always high. The same behavior was noticed in the titration of coumaric acid, and it is possible that the hydroxyl group, having phenolic functions, may, in this case, influence the reaction, though it is well known that salicylic acid, also an orthohydroxy acid, gives very exact titration values. But the aromatic oxy-acids show a varying behavior in this respect, as already noted by Traube,¹ and a further discussion of this point is reserved for a subsequent communication.

Titration:

1. Coumarin, 1.05 g. Heated one hour at 100° with 26.3 cc. 0.5 *N* alcoholic KOH, then 25 cc. water added, and immediately titrated.

Time.....	0	10 min.	1 hr.	2 hr.	18 hr.	24 hr.	114 hr.	162 hr.
Total 0.5 <i>N</i> HCl.....	10.9 cc.	12.0 cc.	14.0 cc.	15.5 cc.	18.2 cc.	20.9 cc.	24.0 cc.	24.2 cc.
Coumarinic acid % ..	107.0	99.4	85.5	75.1	56.3	37.5	15.9	14.9

The alcohol was now evaporated, the solution chilled, the coumarin filtered off, and washed. On standing, the solution became again alkaline, and after 5 days appeared to have reached equilibrium, showing a total of 25.15 cc. 0.5 *N* acid, or 8% coumarinic acid. The solution was now extracted with ether, after which it became slightly alkaline.

Finally, neutrality was reached with 25.25 cc. 0.5 *N* acid, or 7.3% of coumarinic acid. In the solution, evaporated till free from coumarin, no coumaric acid could be detected.

2. Coumarin, 2.019 g., 50 cc 0.5 *N* alc. KOH, heated 2 hours. Titrated without addition of water, and the solution heated at 90–100°.

Here, immediate titration showed 101.9% acid, with equilibrium after 48 hours, at 19.8% acid.

3. Coumarin, 2.077 g., 25 cc. 0.5 *N* alc. KOH, heated 2 hours. Here, although the amount of alkali was insufficient for complete hydrolysis, the solution was still alkaline, and indicated 61% coumarinic acid.

4. Limettin, 2.073 g., 40 cc. 0.5 *N* alc. KOH, heated 2 hours.

Time.....	0	4 hrs.	20 hrs.	44 hrs.	60 days
Total 0.5 <i>N</i> HCl.....	19.4 cc.	23.7	28.7	31.9	34.2
Limettinic acid %.....	102.3	80.9	56.1	40.2	28.8

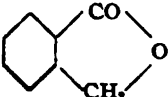
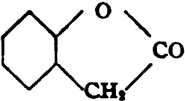
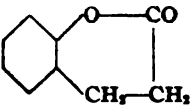
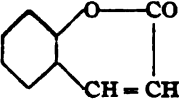
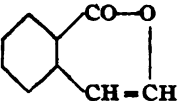
At the end of 4 hrs. limettin commenced to separate in fine needles.

These titrations, of course, give merely a "sketch" of the hydrolysis, no attempt having been made to secure uniformity of conditions.

¹ *Ber.*, 31, 1566 (1898).

Thus, in accordance with the "Spannungs-Theorie" of Baeyer, according to which the simple five atom ring is the most stable, the lactones in the fatty series are also the most readily formed and exhibit the greatest stability.

In the aromatic series, where the benzene and the lactone rings have two atoms in common, somewhat different conditions prevail. For example:

	γ lactone (phthalide)	Not formed spontaneously. Acid stable to 100°.
	γ lactone (keto-hydro-coumarone)	Not formed spontaneously. Acid stable to 137°.
	δ lactone (hydro-coumarin)	Not formed spontaneously. Acid stable to 100°(?).
	δ lactone (coumarin)	Formed spontaneously. Acid unknown.
	δ lactone (iso-coumarin)	Unstable. Acid unknown.

It is evident that a five-ring, of which two atoms also form part of a benzene ring, is under an internal tension rather different from that existing in a simple ring. It is also apparent, from the dissimilarity of coumarin and iso-coumarin, that some unknown factor renders the configuration of the former an especially favorable one.

Coumarinic acid has the combined functions of a phenol and a cinnamic acid, and we may consider the coumarin formation as analogous to the ester reaction between phenol and cinnamic acid. But the favorable spacial relations cause the former reaction to occur spontaneously, even in alkaline solution, while in the latter case, no reaction takes place even in the presence of acid catalyzers.

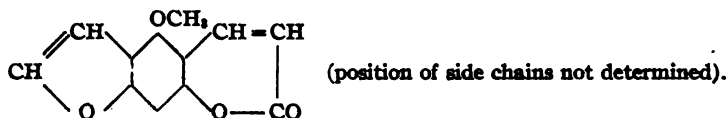
Recognition of Coumarins.

Although the coumarin formation in alkaline solution cannot be considered as strictly characteristic, inasmuch as other lactones are known to exhibit the same behavior, though to a much less degree, it is yet allowable to assume that, in cases where this peculiar reaction is observed, some member of the coumarin series is probably present.

For example, it can hardly have escaped the attention of anyone who

has had occasion too make the usual ester determination on the oil of bergamot, that the end reaction, on titration after saponification, is not sharp. If the solution be set aside, it will be found, after a short time, again alkaline, and will require 0.2 to 0.3 cc. 0.5 *N* acid for neutralization. On standing, the alkaline reaction reappears, exactly as described for coumarin. To reach permanent neutrality may require 48 hours or more, and the difference between the first and final values may amount to 1 or 2%, if calculated as linalyl acetate.

Other oils containing esters, such as lavender, peppermint, birch, pine-needle, etc., which have been *distilled*, do not show this behavior. Bergamot, however, is an *expressed* oil, and contains 5-6% of nonvolatile matter. In the latter must be found the cause of the phenomenon, and, in fact, the crystalline "bergaptene," $C_{15}H_{14}O_4$, isolated from bergamot residues by Mulder,¹ and studied by Pomeranz,² is formulated by the latter as a methoxy-coumaron-coumarin, derived from phloroglucin, and having possibly the structure



In addition to coumarin, bergaptene, limettin, umbelliferon, daphnetin, aesculetin, "chrysotropic acid," already identified as natural products, it appears very probable that other coumarins are yet awaiting recognition. Possibly an example may be found in the "xanthoxylin" of H. M. Gordin.³

Gordin isolated from the bark of the northern prickly ash (*Xanthoxylum fraxineum*), a crystalline compound, $C_{15}H_{14}O_4$, with melting point at 132°. He showed the presence of one methoxyl group, but could not determine the nature of the other three oxygen atoms, deciding rather against a lactone formula. Yet he found xanthoxylin to exhibit exactly the behavior on hydrolysis which I have described for coumarin. On treatment with excess of alcoholic alkali, it takes up slightly more than would be required for a monobasic acid. On standing the alkali is slowly liberated, and may be titrated, etc., until the entire amount of xanthoxylin has been set free.

In spite of Gordin's reasons for rejecting the lactone formula, the writer is inclined to believe that xanthoxylin will be found to be a coumarin, and, indeed, possibly a homolog of bergaptene, as a comparison of the formulae will show.

¹ *Ann.* 31, 70 (1839).

² *Monatsh.*, 12, 380 (1891).

³ *THIS JOURNAL*, 28, 1649 (1906).

Finally, it may not be superfluous to recall the fact that many substances, of great interest by reason of their physiological properties, have been found to possess a lactone structure. Cantharidin, anemonin, aesculin, digitoxin, helenin, santonin, picrotoxin, strophanthin, sedanolid, artemisin, are examples, and it seems not unlikely that there may be some intimate causal relation between the mobility of the lactone ring and the observed physiological activity.

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SPECTROPHOTOMETRIC STUDY OF COPPER COMPLEXES AND THE BIURET REACTION.

BY PHILIP ADOLPH KOBER AND ARTHUR B. HAW.

Received October 1, 1915.

CONTENTS.—I. Introduction. II. Absorption in the ultraviolet: (a) Technic; (b) Results. III. Absorption in the visible spectrum: (a) Technic; (b) Results. IV. General discussion. V. Summary.

I. Introduction.

In the first paper¹ on the configurations of the copper complexes and their relation to the biuret reaction, it was found that the copper complexes of amino derivatives and other similar substances could be divided, according to their color, into three classes. (1) Blue, (2) purple—called “semi-biuret”—and (3) red—called “biuret.” The first class was also characterized by the fact that there were in each complex 2 nitrogen groups so placed, that by forming “stable” rings,² they could combine with the copper. The complexes of the second class had 3 such groups and the third class had 4.

All told, 114 substances were found which fitted in this classification, of which 89 were studied by the authors. In short, all of the data found pointed to but one explanation, *i. e.*, that the copper in the red complexes was the central atom and that 4 nitrogen groups were combined with it coördinately in the sense used by A. Werner. The nitrogen groups could be either amino, imino, imide, or amide. As the coördination number of copper is four, the purple complexes probably contain besides 3 nitrogen atoms, one aquo or hydroxy group attached to the copper. The bluish tint of these purple complexes is undoubtedly due to the latter groups.³ Similarly the blue complexes may have two hydroxy groups attached to the copper.

That the nitrogen plus copper is not a red producing chromophore and that the red colors are produced, simply by removing the blue produc-

¹ P. A. Kober and K. Sugiura, *Am. Chem. J.*, 48, 383 (1912); also original communications, 8th Intern. Congr. Appl. Chem., 6, 165 (1912).

² 4, 5, or 6 membered rings.

³ See discussion on page 471.

ing hydroxy or aquo groups, yielding the true color of cupric copper in a nonhydrated condition seems probable, but cannot be decided definitely yet. What conditions are necessary, either in a nitrogenous substance or in the solvent, to permit such coördinated copper compounds to be possible and to be stable in aqueous solutions has already been considered in a previous paper.¹

The theory has already proven to be useful, as a new complex of copper and biuret was found, with its help, to exist in solution, and whose isolation and analysis published subsequently by Ley and Werner² proved it to have the composition then formulated. The next steps in establishing this theory are: (1) to show that the absorption spectra agree with the macroscopical observations, that these colors can be divided into three classes and only three, and that the absorption spectra of a class are practically identical, and (2) to show that it really is the nitrogen groups themselves and not groups associated with the nitrogen, as for example some have supposed, oxy or hydroxy groups, that produce these colors. As the title indicates this paper deals mostly with the absorption spectra of these complexes, but certain points of the second step are also brought out.

II. Absorption in the Ultraviolet.

(a) **Technic.**—The Hilger quartz spectrograph³ size *c*, was used in connection with a sparking outfit⁴ consisting of 1/4 k. w. rotary converter, transformer (giving about 15,000 volts) and condenser, which gave a strong spark between the electrodes. As the details of the arrangements have appeared in another paper⁵ they are not given here.

(b) **Results.**—The following photographs,⁶ Fig. 1, show that the absorption is general and that variations in the constitution of these complexes cannot be followed by quantitative ultraviolet spectroscopy.

The marked general absorption in the ultraviolet, in harmony with the observations of Ley and Legge,⁷ is due, no doubt, to the copper in the complex. Whether the quantitative work in the ultraviolet may be of more service in this connection cannot be stated now, but since the classification of the complexes depends on the variation of the visible spectrum, quantitative measurements in this region were then made.

¹ *Loc. cit.*

² *Ber.*, 46, 4040 (1913). The authors state that they had isolated the compound before the appearance of Kober and Sugiura's paper. The results however for "external reasons" were not published till more than a year later.

³ Made by Adam Hilger, Ltd., London, England.

⁴ Made by Clapp-Eastham Co., Cambridge, Mass.

⁵ Kober, *J. Biol. Chem.*, 22, 433 (1915).

⁶ We are indebted to Mr. Walter Eberlein, for making these photographs (taken March 7-9, 1914).

⁷ *Ber.*, 38, 70 (1915).

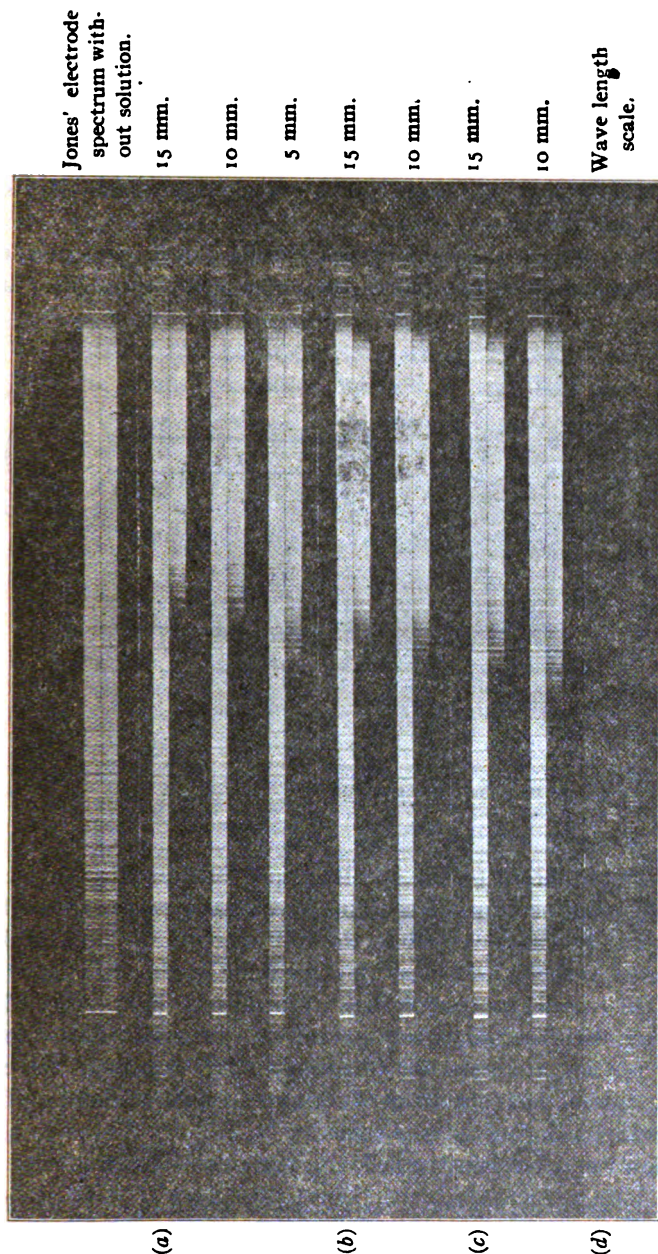


Fig. 1.

- (a) Blue complex; alanyl-glycine copper (0.110 g. CuO in 100 cc.).
 (b) Purple complex; alanyl-leucyl-glycine copper (0.062 g. CuO in 100 cc.).
 (c) Red complex; N-amino-capronyl-diglycyl-glycine copper (0.054 g. CuO in 100 cc.).
 (d) Wave length scale. Made especially to fit this instrument.

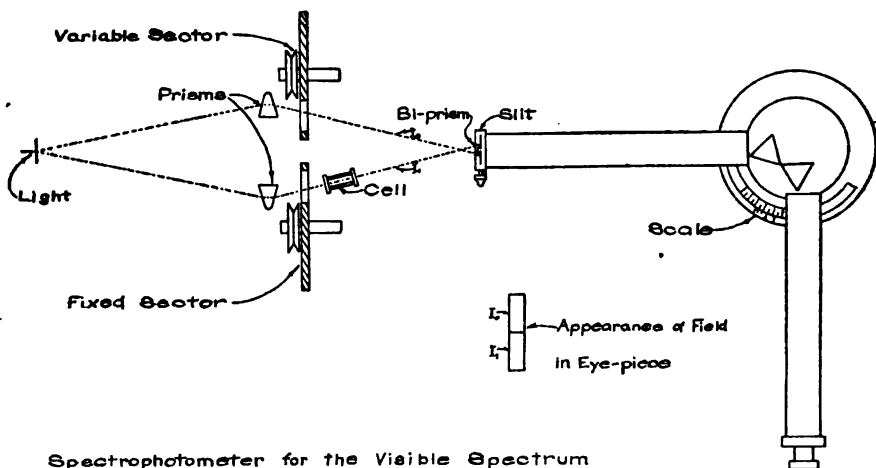
III. Absorption in the Visible Spectrum.

(a) **Technic.**—As the apparatus used represents economy in instruments, was simple and effective, a description may be worth while. A Hilger¹

¹ Made by Adam Hilger, Ltd., London, England.

sector photometer and an ordinary high dispersion spectroscope¹ comprise the essential parts of the apparatus. The photometer was designed for work in the ultraviolet, according to the photographic method of Victor Henri. It had originally a speed of 120 revolutions per minute, but by suitable gearing, this was increased to over 2000 revolutions² per minute, so that when the spectrum was seen in the eye-piece, not the slightest trace of vibration and flicker was obtained.

As may be seen in Fig. 2, the light from a Nernst glower, was divided, by means of two prisms, into two paths, the upper going through a cali-



Spectrophotometer for the Visible Spectrum
Hilger Photometer and Browning Spectroscope

Fig. 2.

brated variable sector direct to the spectroscope. This path represents the light entering the medium (I_0). The lower path passes through a fixed sector, whose aperture is equal to the full aperture of the variable, after which it goes through the absorbing medium in the cell, into the spectroscope. This path represents the transmitted light (I_1). The two paths produce with the aid of a bi-prism³ two spectra in close juxtaposition and by putting a narrow slit (made from stiff paper) in the eyepiece, a small section of each spectrum is seen and a field resembling that of an ordinary wedge colorimeter is obtained.

After a solution was placed in the cell, the variable sector was changed

¹ Made by John Browning, London, England; kindly loaned to us by Dr. J. T. W. Marshall, for which we wish to express our thanks.

² To prevent vibrations to the spectroscopic table, the photometer was mounted on sections of rubber, made by cutting down rubber stoppers to about $\frac{1}{4}$ inch thickness.

³ The sleeve with slit and bi-prism, belonging to the quartz spectrograph for quantitative work in the ultraviolet, were put into the place of the original sleeve and slit, as the two sleeves were practically of the same size.

step by step, from full aperture to 90, 80, 70, 60, 50, 40, 30, 20 and 10% transmission of light. At each step the eye-piece was moved over the whole visible spectrum and the spectroscope scale was read at each point where the two spectral sections were of equal intensity. Thus in 10 settings, the whole absorption curve was quantitatively determined.

The cell was a Schmidt and Haensch 25 mm. polariscope tube, with screw ends, so that the solutions were not open to contamination from the air, *especially from carbon dioxide*, during the measurements. When the two instruments were in position, with distilled water in the cell, the two spectra showed equal intensity throughout.

The basis of this photometric method, Talbot's law of Rotating Sectors, while doubted occasionally in the past, has been shown by E. P.

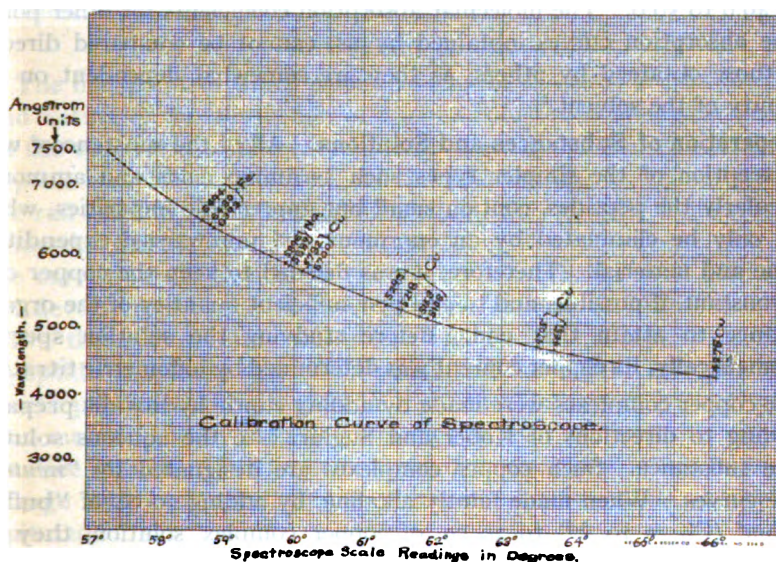


Fig. 3.

Hyde¹ and others, to be accurate within experimental error, and is now fairly well accepted by photometrists.

The wave lengths corresponding to the readings of the spectroscope scale were determined by noting the position of some standard lines in the spectrum of the iron and copper arc and the sodium flame. These readings were then plotted with the wave lengths, and from the curve obtained, Fig. 3, any scale reading could be expressed at once in Angstrom Units.

The photometric results of this paper are probably only accurate to within 2%, as not more than two readings were made on an average for

¹ Bureau of Standards, *Bull.* 26. For white light he found Talbot's law to hold within 0.2% and for colored lights the accuracy was not far from that figure.

each point, although the usual photometric precautions of working in a dark room and shielding the eyes from any glare, were observed. Taking the maximum absorption of the glycine and ammonium complex of copper as standards, our results compare favorably with those obtained with other instruments. Using the formula $\epsilon = 1/m.d \log I_0/I_1$, where m equals the gram molecules of substance, d equals the thickness of absorbing medium in centimeters, I_0 the light entering the medium, and I_1 the transmitted light, we found the molecular absorption coefficient ϵ for the glycine copper complex to be 40. Using a Koenig-Marten spectrophotometer, Ley and Legge¹ found 42. For the ammonium copper complex, we found the coefficient to be 51. Whereas Ley and Legge, and Hantzsch,² also using a Koenig-Marten spectrophotometer, found it to be 49.6 to 50.0. The molecular absorption coefficients for other points on the absorption curves, obtained by us, cannot be compared directly with those obtained by others, as they are somewhat dependent on the alkalinity of the solvent.³

Preparation of Substances and Solutions.—All of the substances⁴ with the exception of the simpler types such as amino acids and ammonia, particularly the peptides, contain small but appreciable impurities, which could only be eliminated by an enormous and unrewarded expenditure of time and material. Therefore, it was decided to keep the copper content constant, if possible, and to add just sufficient quantity of the organic substance to attain that end. Before studying the solution spectrophotometrically, its copper content was determined by iodometric titration.

The copper complexes were made by adding cupric hydroxide, prepared according to directions of Kober and Sugiura,⁵ to the aqueous solution of the substance. Such copper complexes are designated by "neutral" in the curves. When made faintly alkaline, by adding 20 cc. of "buffer" solution⁶ ($C_H = 10^{-8.8}$) to 30 cc. of copper complex solution, they are designated as "buffer."⁷ When made strongly alkaline by adding from 3 to 10 cc. of normal carbon dioxide free sodium hydroxide, to 25 cc. of copper complex solution, the curves are designated as "alkaline."

Previous work in the quantitative study of absorption in the visible

¹ *Ber.*, 48, 70 (1915).

² Hantzsch and Robertson, *Ibid.*, 42, 2135 (1909).

³ See discussion on p. 463.

⁴ Taken from the collection of amino acids, peptides and their derivatives purchased from the estate of the late Dr. A. H. Koelker, who made and gathered most of the substances, while working in the Fischer, Abderhalden, and Johns Hopkins Laboratories.

⁵ *THIS JOURNAL*, 35, 1557 (1913).

⁶ *Ibid.*, 1558.

⁷ The lack of a potentiometer prevented us from determining accurately the OH concentrations in the final solutions.

has been limited to the measurement of the absorption coefficients at certain wave lengths¹ and only recently Henri measured and plotted the whole absorption curve in his ultraviolet work. For the reader these tables of absorption coefficients are difficult to compare, although for accuracy this method of presentation is excellent. As curves, accurate to within the limits of experimental error, can be constructed, we propose to give all our data in the form of curves. It will present the results more simply for the average reader, while those interested in the details can by little effort, obtain all the accuracy possible, because the accuracy of the curves will not be affected by their reduction in the Journal.

(b) **Results.**—The results shown in the following figures, 4, 5, 6, 7 and 8, were obtained at room temperature and are given without comments, as these are brought out in the discussion.

IV. General Discussion.

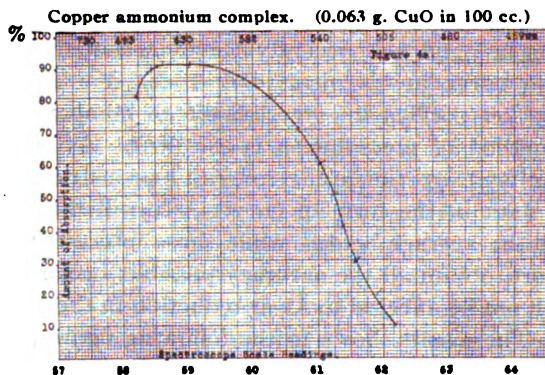
The first point to which attention may be directed, is that the amount and nature of the absorption of a given complex is somewhat dependent on the concentration of hydroxyl ions. As may be observed, in the tetrapeptide complexes, 5c, 6c and 7a, the weaker alkali only faintly develops the red color, while in the stronger alkali, the red color is most fully developed. On the other hand, in the tripeptides the reverse is true. In the curves 5a, 5b, 6a and 6b, the weaker alkali is the most favorable for the development of the purple or semi-biuret color, and the stronger alkali shifts the color towards the blue. The variations in color of the blue dipeptide complexes, with the alkalinity of the solvent, were not studied, spectrophotometrically, owing to the lack of opportunity, but we know that macroscopically there is no change of color, with weakly or strongly alkaline solution. In the amino-acid blue complexes, there is no visible change with weak alkali, but in strong alkali most of the copper is precipitated.²

From this we can safely conclude that each class of complexes, or at least each complex, has a certain concentration of OH ions at which the maximum development of red color is obtained.

The results give three types of absorption curves: (1) *Blue complexes:* the absorption beginning at about 480 $\mu\mu$ and reaching a number maximum at 630 $\mu\mu$, as in curves, 4a, 4b, 4c and those marked "neutral" in 5a, 5b, 5c, 6a, 6b, 6c and 7a. (2) *Purple or semi-biuret complexes:* absorption beginning at about 459 $\mu\mu$ and reaching a maximum at 540 $\mu\mu$, as in curves marked "buffer" in 5a, 5b, 6a and 6b. (3) *Red or biuret com-*

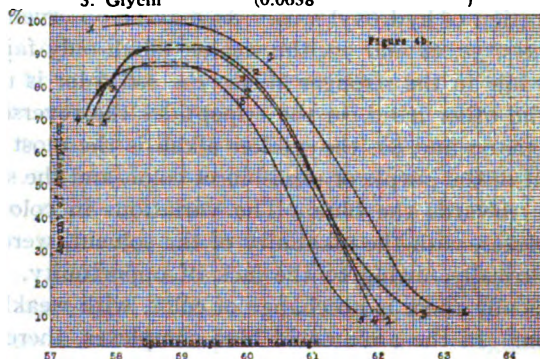
¹ See Hantzsch, Ley and others, *Loc. cit.*

² Kober and Sugiura, *THIS JOURNAL*, 35, 1572 (1913), showed that the stability, or inversely the precipitability, of the complexes, under certain conditions is in the same order; tetrapeptide complexes precipitate Cu on an average 9.2%; tripeptides, 10.8%; dipeptides, 17.3%; amino acids, 86.5%.



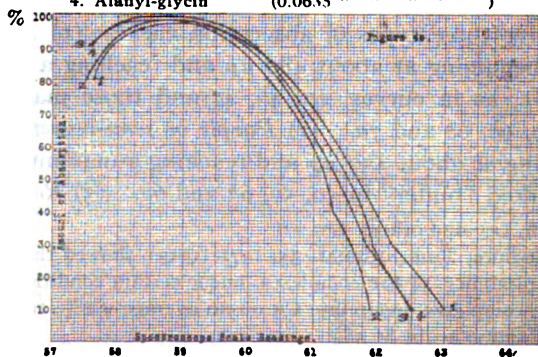
Amino acid copper complexes.

1. Histidin di-HCl (0.0637 g. CuO in 100 cc.)
2. Glutamic acid (0.0633 " " " " " ")
3. Aspartic acid (0.0617 " " " " " ")
4. Alanin (0.0635 " " " " " ")
5. Glycin (0.0638 " " " " " ")



Dipeptide copper complexes.

1. Glycyl-tryptophane (0.0637 g. CuO in 100 cc.)
2. Glycyl-leucin (0.0640 " " " " " ")
3. Amino-butyl-glycin (0.0636 " " " " " ")
4. Alanyl-glycin (0.0635 " " " " " ")

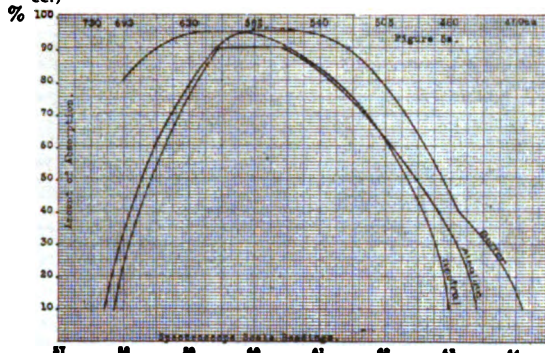


(1) *Tripeptide complexes.*

Alanyl-glycyl-glycin copper (neutral solution; 0.0640 g. CuO in 100 cc.)

Alanyl-glycyl-glycin copper (buffer solution; 0.0316 g. CuO in 100 cc.)

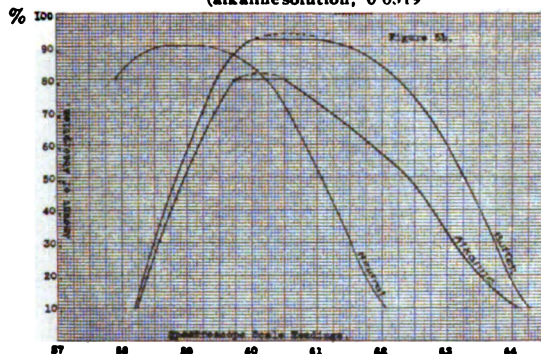
Alanyl-glycyl-glycin copper (alkaline solution; 0.0316 g. CuO in 100



Di-glycyl-glycin copper (neutral solution; 0.0527 g. CuO in 100 cc.)
 " " " (buffer solution; 0.0319 " " " " "
 " " " (alkaline solution; 0.0319 " " " " ")

"	"	"	(buffer solution; 0.0319 "	"	"	"	"	"	"
"	"	"	(alkaline solution; 0.0319 "	"	"	"	"	"	"

% 100

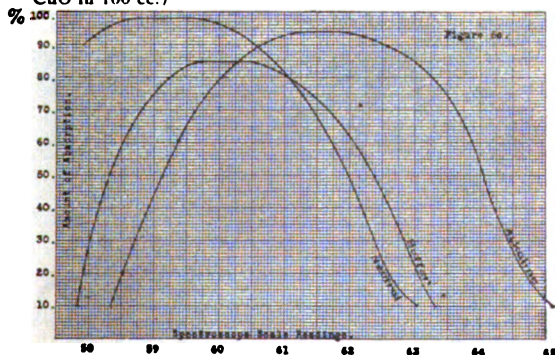


(2) *Tetrapeptide complexes.*

N-amino-caproyl-di-glycyl-glycin copper (neutral solution; 0.0629 g. CuO in 100 cc.)

N-amino-caproyl-di-glycyl-glycin copper (buffer solution; 0.0311 g.
CuO in 100 cc.)

N-amino-caproyl-di-glycyl-glycin copper (alkaline solution; 0.0310 g.
CuO in 100 cc.)

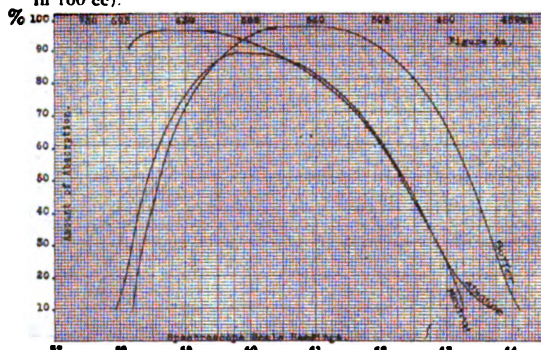


(1) *Tripeptide complexes.*

Amino-butyl-glycyl-glycin copper (neutral solution; 0.0633 g. CuO in 100 cc.)

Amino-butyl-glycyl-glycin copper (buffer solution; 0.0317 g. CuO in 100 cc.)

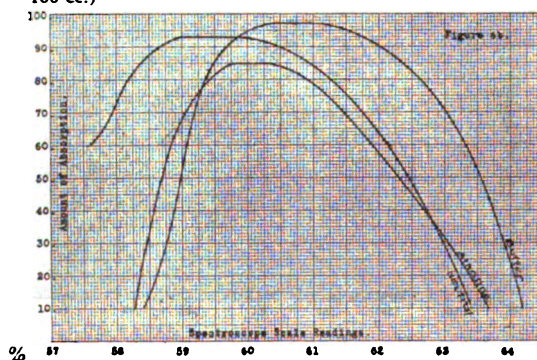
Amino-butyl-glycyl-glycin copper (alkaline solution; 0.0317 g. CuO in 100 cc.)



Leucyl-alanyl-glycin copper (neutral solution; 0.0639 g. CuO in 100 cc.)

Leucyl-alanyl-glycin copper (buffer solution; 0.0311 g. CuO in 100 cc.)

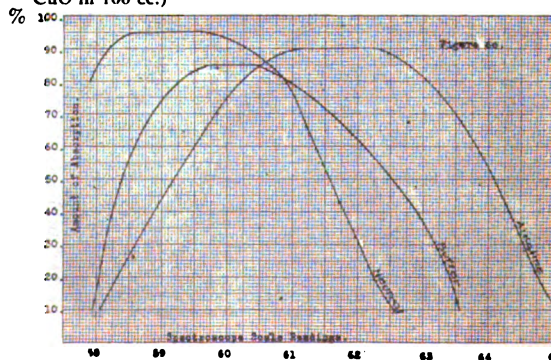
Leucyl-alanyl-glycin copper (alkaline solution; 0.0318 g. CuO in 100 cc.)

(2) *Tetrapeptide complexes.*

Amino-butyl-di-glycyl-glycin copper (neutral solution; 0.0634 g. CuO in 100 cc.)

Amino-butyl-di-glycyl-glycin copper (buffer solution; 0.0318 g. CuO in 100 cc.)

Amino-butyl-di-glycyl-glycin copper (alkaline solution; 0.0319 g. CuO in 100 cc.)

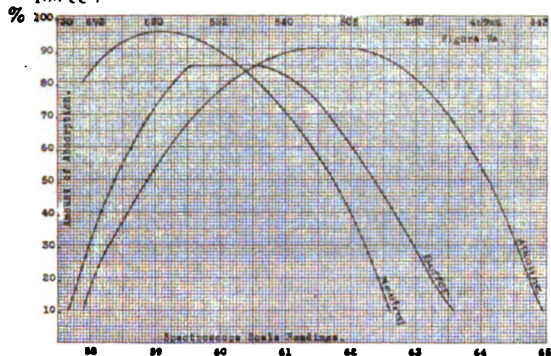


(2) *Tetrapeptide complexes.*

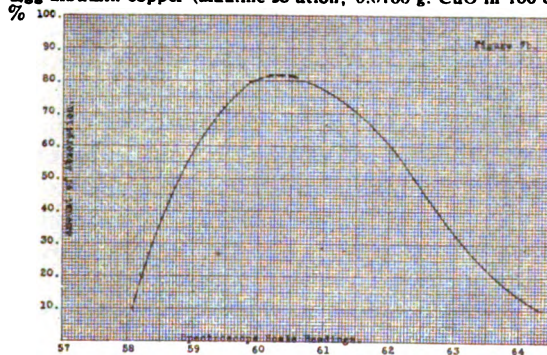
Alanyl-di-glycyl-glycin copper (neutral solution; 0.0630 g. CuO in 100 cc.)

Alanyl-di-glycyl-glycin copper (buffer solution; 0.0316 g. CuO in 100 cc.)

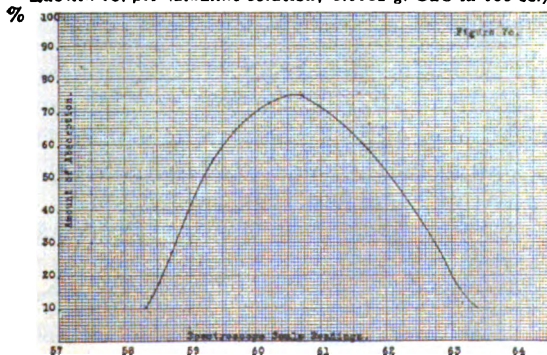
Alanyl-di-glycyl-glycin copper (alkaline solution; 0.0317 g. CuO in 100 cc.)



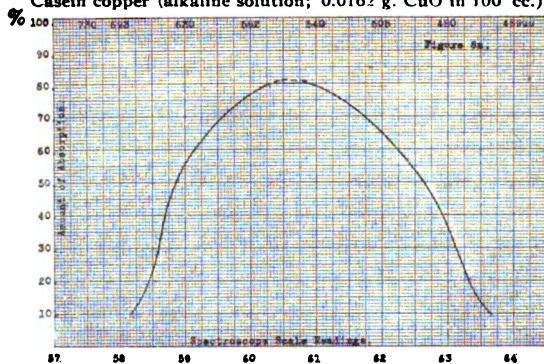
Egg albumin copper (alkaline solution; 0.0160 g. CuO in 100 cc.)



Edestin copper (alkaline solution; 0.0162 g. CuO in 100 cc.)

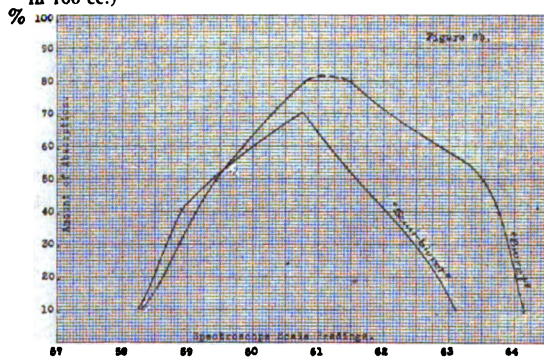


Casein copper (alkaline solution; 0.0162 g. CuO in 100 cc.)



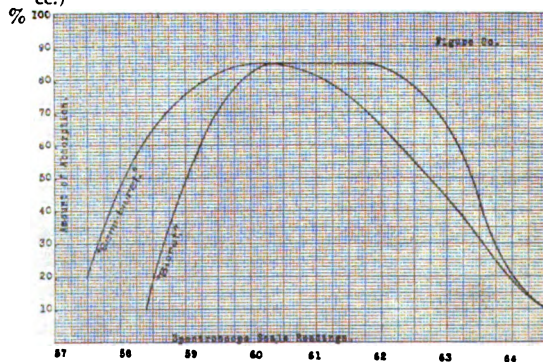
Witte peptone with copper ("semi-biuret") (alkaline solution; 0.0166 g. CuO in 100 cc.).

Witte peptone in excess ("biuret") (alkaline solution; 0.0162 g. CuO in 100 cc.)



Cu(biuret)₂ ("biuret") (alkaline solution; 0.0628 g. CuO in 100 cc.)

Cu(biuret) ("semi-biuret") (alkaline solution; 0.0628 g. CuO in 100 cc.)



plexes: absorption beginning beyond 443 $\mu\mu$ and reaching a maximum at 505 $\mu\mu$, as in curves marked alkaline in 5c, 6c and 7a, 8c.

The results with diglycyl-glycine also show that in the "buffer" solution the semi-biuret color is as strong as with the other tripeptides, corroborating spectrophotometrically a former observation.¹ Therefore, E. Fischer's statement that this peptide does not give a biuret reaction and is an exception to the other tripeptides, is shown to be incorrect. This error is a result of the fact that he used and recommended strong alkali for biuret reactions. *No doubt negative biuret reactions with other substances, which theoretically ought to be positive, are often due to unfavorable amounts of alkali used.*

Although there are variations due to unfavorable alkalinity and to some extent to impurities, yet the results show three types and only three types of absorption.

Biuret Reaction of Proteins.—In 7b, 7c, 8a and 8b, the absorption curves of a number of protein complexes are shown. Similarly as with the peptides, a suitable amount of protein was treated with an *excess of cupric hydroxide*, but in a strongly alkaline solution. After filtering and estimating the copper, the absorption was determined.

As the results show, the curves are practically the same as were obtained with the tripeptides, except the apparent absorption is less. On calculating the molecular absorption coefficient, however, for wave length 540 $\mu\mu$, the amount of absorption with the alkaline protein complexes is found to be about the same as with the tripeptide complexes in "buffer" solution, *i. e.*, they give a semi-biuret color.

TABLE I.

	% Absorption.	Coefficient.		% Absorption.	Coeff.
Alanyl-glycyl-glycine.....	94	122	Casein.....	79	136
Diglycyl-glycine.....	93	116	Egg albumin.....	77	128
Leucyl-alanyl-glycine.....	97	152	Edestine.....	71	108
Amino-butyl-glycyl-glycine....	96	140			
	—	—		—	—
	Av., 95	133		76	124
			Peptone (semi-	64	188
			(biuret) ..	80	140

With Witte peptone, the results are less certain, as the substance is a crude and colored mixture, and may contain interfering substances. It will also be observed that an error of 1% in the measurement of absorption at these points is multiplied from 4 to 10 times in the molecular absorption coefficient. The greatest accuracy in determining the coefficient, is obtained by keeping the absorption at 50%.

These results support, if they do not prove two points: (1) *that the so-called "biuret reaction," a test used for the past half century for detecting*

¹ THIS JOURNAL, 35, 1571 (1913).

proteins qualitatively, is no other than a complex formation with copper and, therefore, as far as color formation is concerned, no decomposition of the protein is involved.¹ (2) That the protein configurations are such that permit only 3 nitrogen groups to form rings with copper; and, therefore, the protein molecule must be aggregated, and is not in the form of long free chains or branches of peptides or conjugated amino acids. This is supported by other facts; Kober and Sugiura² showed that these native proteins give no test for free amino acids, and Van Slyke and Birchard³ showed that most of the amino groups—and, therefore, also the carboxyl groups—are conjugated.

The biuret reaction made in this way, *i. e.*, saturating the protein substance with copper, and determining the nature and the amount of absorption as well as the amount of copper combined, may increase the value of the copper technic⁴ in studying the constitution of proteins and their derivatives. Thus, for example, it may be possible by estimating the absorption at wave lengths which are characteristic of each type, to determine in mixtures how much of each type is present. For example (1) wave length 693 $\mu\mu$ possibly could be used for estimating the amount of blue or dipeptide complexes. (2) Wave length 560 $\mu\mu$ could possibly be used for both the purple (tripeptide) and the red (tetrapeptide), while (3) wave length 455 $\mu\mu$ might be used for the latter alone. Subtracting the amount of copper found by (3) from that found with (2), would give the amount of tripeptide complexes.

Some Evidence For these Configurations.—It is reasonably certain, that the direct cause of these red color reactions with copper has nothing to do with the hydrocarbon part of the substance, but is due either to the oxygen or nitrogen groups, or to both. It is of utmost importance for practical purposes, aside from the general interest in these complexes, to know to what groups in the substance this coloration is due. The amount of color in the biuret or semi-biuret complexes is about 13 times as strong as the color of ordinary copper salts, such as the blue sulfate.

If the color were due to the oxy or hydroxy groups alone, would this agree with the following facts? (1) That copper compounds of substances containing no nitrogen, but oxy or hydroxy groups, such as glucose, fructose, lactose, galactose, maltose, glycerol, and lactic acid *are quantitatively* and tartaric, citric, and oxalic acid, *from 50 to 90% decomposed*, in a weakly alkaline solution⁵ in which all complexes of amino acids, peptides and other

¹ The strong alkali usually used for making this test does no doubt cause hydrolysis of the protein, but this is purely incidental.

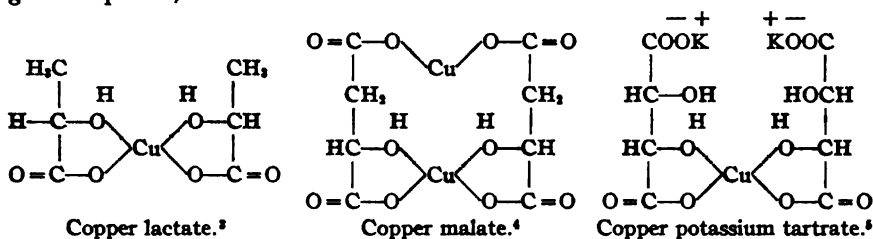
² THIS JOURNAL, 35, 1580 (1913).

³ J. Biol. Chem., 16, 539 (1914).

⁴ THIS JOURNAL, 35, 1563-4 (1913).

⁵ Kober and Sugiura, *Ibid.*, 35, 1562 (1913).

protein derivatives are *perfectly stable*.¹ Similarly that stability of these oxy and hydroxy complexes in strong alkali² is not at all comparable to those of the peptide or protein complexes. (2) That thus far no red colored complexes of copper, in aqueous solutions, have ever been found containing only oxygen groups. The specificity accorded heretofore to the biuret reaction for proteins is in harmony with that fact. (3) That a number of copper complexes of oxy or hydroxy substances, which have been studied and which have the same possible ring configuration as these nitrogen complexes, are *blue*.



To sum up: *oxy or hydroxy complexes of copper, no matter what configuration they may possess, are all blue or green, and never red, and are characterized by their relative instability in alkaline solutions.*

That the red colors are due to nitrogen groups, the following facts tend to prove: (1) Substances possessing *no oxygen and only nitrogen* give a red biuret reaction, *e. g.*, diguanidine copper.⁶ (2) Complexes containing a *deficiency of oxygen groups* (more than two groups whether it be oxygen or nitrogen, are necessary for these biuret colors) but sufficient nitrogen groups, give a red biuret reaction, as for example dicyanodiamidine copper,⁷ semi-biuret copper,⁸ 21 crystalline complexes of Tschugaeff,⁹ and others, all of which contain two oxygen and three or four nitrogen groups. (3) Finally, *the great parallelism between the number of nitrogen groups available for the combination with copper, and the red colors*; that the amount of red color in a complex is a function, as is shown in this paper spectrophotometrically, of the number of nitrogen groups,—up to four—attached to the copper atom. Thus 68 amino acids and peptides, 21 chloro and bromo derivatives, studied by Kober and Sugiura, 25 amino substances prepared by Emil Fischer and collaborators (not included by K. and S.),

¹ THIS JOURNAL, 35, 1551-7 (1913).

² *Ibid.*, 1563 and 1572.

³ Paul Calame, *Z. physik. Chem.*, 27, 401-20 (1908).

⁴ *Ibid.*

⁵ Kahlenberg, *Z. physik. Chem.*, 17, 590 (1895).

⁶ Tschugaeff, *Ber.*, 40, 1977 (1907).

⁷ Tschugaeff, *Ibid.*, 40, 1977; 38, 2904; 37, 1480.

⁸ Kober and Sugiura, *Am. Chem. J.*, 48, 402 (1912); Ley and Werner, *Ber.*, 46, 4040 (1913).

⁹ Tschugaeff, *Loc. cit.*

21 complexes of Tschugaeff mentioned above give 135 different complexes which seem to be in harmony with this theory of biuret reaction. This list is by no means complete.

Having thus shown what seems fairly conclusively, that the red color of these copper complexes is due to the presence of nitrogen groups alone, the next step is to find what the other details of these complexes are, and how the complexes are formed. Since experimental evidence on all points is not available, and on some points evidence is wholly lacking, our discussion on these questions, as well as our reply to recent criticism will be reserved for a subsequent paper.

V. Summary.

1. The absorption in the visible spectrum, of copper complexes of amino acids, peptides and proteins was studied quantitatively, in neutral and alkaline solutions.
2. From the nature and the amount of absorption, considerable support was found for the theory of biuret reaction proposed by Kober and Sugiura.
3. The biuret reactions with proteins seems to be nothing more than ring formations of the copper with the nitrogen groups.

HASTINGS-ON-HUDSON, N. Y.

[CONTRIBUTION FROM COLUMBIA UNIVERSITY AND THE HARRIMAN RESEARCH NO. 258.]

THE PHOSPHORIC ACID IN STARCH.

By JOHN H. NORTROP AND J. M. NELSON.

Received November 20, 1915.

Up to the present time no definite evidence has been brought forth as to whether the phosphoric acid present in starch is in chemical combination or not. Ford,¹ Fernbach,² Fernbach and Wolff,³ Malfitano,⁴ Malfitano and Moschkoff,⁵ Fouard,⁶ Thomas,⁷ Grewzewska⁸ and others, employing a variety of methods such as precipitation with alcohol, acetone, freezing or dialysis, etc., all were unable to completely free the starch from its accompanying phosphorus.

Samec,⁹ seems to have shown quite conclusively that the starch granules are not homogeneous and that the phosphorus is associated with the exterior of the grains (amylopectin). He further states that the phosphoric acid and the amylopectin are chemically combined in the form of an amylophosphoric acid, since the only way to account for the decrease

¹ *J. Soc. Chem. Ind.*, 23, 414 (1904).

² *Compt. rend.*, 138, 428 (1904); 155, 617 (1912).

³ *Ibid.*, 140, 1403 (1905).

⁴ *Ibid.*, 143, 400 (1906).

⁵ *Ibid.*, 150, 711 (1910).

⁶ *Ibid.*, 144, 501 (1907); 146, 285 (1908).

⁷ *Biochem. Bull.*, 3, 407 (1914).

⁸ *Compt. rend.*, 152, 785 (1911).

⁹ *Kolloidchem. Beihefte*, 3, 123 (1911); 4, 133 (1912); 5, 141 (1913); 6, 23 (1914).

in viscosity and cataphoresis, and increase in solubility, osmotic pressure and activity, when starch solutions are heated or allowed to stand is by the hydrolysis, with the liberation of free phosphoric acid from a compound of this type. Samec measured what he considered to be the hydrolysis of the amylophosphoric acid, by the increase in the conductivity of the solution. Results obtained independently in this laboratory, however, show that little or no free phosphoric acid is liberated under these conditions and that, therefore, the change in properties of a starch solution under these conditions can not be attributed to the hydrolysis of such an amylophosphoric acid. It was found, on the contrary, that several hours' heating with 10% acid were necessary for the liberation of all the phosphoric as free phosphoric acid. This is in keeping with the behavior of other phosphoric acid esters studied by Fisher,¹ Anderson,² Plimmer,³ and Levene and Jacobs.⁴

The results of the present investigation show: *

First. The phosphorus is chemically combined in the starch grains and cannot be removed by extraction with dilute acid, either in the form of free phosphoric acid or in combination. This shows that its presence cannot be due to contamination with other material present in the potatoes from which the starch used in this investigation was obtained.

Second. A method has been found for the isolation, from partially hydrolyzed starch, of a compound of relatively high phosphorus content, of definite composition and containing a carbohydrate.

Third. This compound differs from Samec's hypothetical amylophosphoric acid in that it is more stable towards hydrolysis.

Fourth. The possibility that the compound is derived from proteins in the starch is shown to be very remote, in view of the small amount of nitrogen present in the original starch and of the fact that acetyl derivatives were obtained that contained phosphorus but no nitrogen.

Experimental.

Determination of Phosphorus.—The sample was decomposed by the Neumann method and the phosphorus precipitated as ammonium phosphomolybdate⁵ and determined by titration with alkali,⁶ formaldehyde being added to remove the ammonia.⁷ The starch used in this investigation was potato flour and was found to contain 0.06% phosphorus by this method.

No phosphate could be extracted by dilute acid, while a known amount

¹ *Ber.*, 47, 3193 (1914).

² *J. Biol. Chem.*, 20, 487 (1915).

³ *Biochem. J.*, 7, 43 (1913).

⁴ *Ber.*, 41, 1905 (1908).

⁵ Hibbard, *J. Ind. Eng. Chem.*, 5, 998 (1913).

⁶ Falk and Sugiura, *THIS JOURNAL*, 37, 1507 (1905).

⁷ Bang, *Biochem. Z.*, 32, 443 (1911).

of phosphate added to the starch before extraction could be completely recovered, showing that the phosphorus is not present as an adsorbed impurity.

Ten grams of starch were stirred twenty-four hours with 500 cc. of 2% hydrochloric acid, filtered, the filtrate evaporated to 150 cc. and the phosphorus precipitated with molybdate as usual. The amount of precipitate was too small to determine. The experiment was repeated with the addition of 0.0064 g. of phosphorus as secondary potassium phosphate to the solution before extraction and resulted in the recovery of 0.00638 g. of phosphorus.

Determination of Nitrogen.—Various figures are given in the literature for the percentage of nitrogen present in potato starch. König¹ gives 0.1%; Fernbach² found 0.018–0.038%; and Samec³ reports a trace. Analysis of 5 g. of the starch used in this investigation gave negative results by the Kjeldahl method. The Dumas method, using a 1 g. sample also gave negative results. A slight coloration was obtained in the nitroprusside test, which was found to be less than that obtained from a mixture of crystallized egg albumin and cane sugar containing 0.1% nitrogen.

Isolation of a Compound of Higher Phosphorus Content.—Born and Nelson⁴ have shown that the phosphorus bearing polysaccharide or invertase undergoes acetolysis in such a way as to increase the percentage of phosphorus. Acetylation of starch, however, led only to the isolation of products containing 0.06–0.13% phosphorus. Since no products containing a higher percentage of phosphorus could be isolated by this method, it was abandoned. The acetyl derivatives were free from nitrogen, so that it seems improbable that the phosphorus was of protein origin.

Acid Hydrolysis.—It was found, however, that starch could be partially hydrolyzed by acid without splitting off more than a small percentage of the total phosphorus and that compounds of relatively high phosphorus content could be isolated from this partially hydrolyzed starch solution.

Ten grams of starch were dissolved in 100 cc. of 10% hydrochloric acid and the solution heated on the water bath until no precipitate was obtained on adding a drop of the solution to alcohol. The solution was then filtered from the precipitate of retrograded starch which always formed and the amount of free phosphoric acid determined in the filtrate by precipitation first with magnesia mixture and then with molybdate. The experiment was then repeated with the addition of a known amount of a

¹ *Nahrungs und Genussmittel*, 3rd ed., I, 626.

² *Loc. cit.*

³ *Loc. cit.*

⁴ *THIS JOURNAL*, 36, 393 (1913).

solution of secondary potassium phosphate to the solution before hydrolysis. The results obtained by difference in this way were the same as those obtained directly, showing that this phosphorus was not retained by adsorption. Only 3-5 % of the total phosphorus could be found in the solution as free phosphoric acid when the starch was hydrolyzed under these conditions. The results of four such determinations are given in Table I.

TABLE I.

Grams starch.	10.	10.	10.	10.
Grams P found.....	0.00023	0.00024	0.00662	0.00664
Grams P added.....	0.0064	0.0064
P from starch.....	0.00023	0.00024	0.00022	0.00024
Per cent. P hydrolyzed.....	3.83	4.00	3.66	4.00

These results render it improbable that the increase in conductivity noticed by Samec, when starch solutions were heated or allowed to stand, was due to the liberation of free phosphoric acid.

Long-continued hydrolysis with acid resulted in the liberation of all the phosphorus as free phosphoric acid. Thus it will be noticed that the starch compound differs from phytin in this respect, since Anderson and others have shown that phytin is completely hydrolyzed only by heating with strong acid under pressure.¹

Ten grams of starch were dissolved in 100 cc. of 10% hydrochloric acid and heated on the water bath with a reflux condenser for fourteen hours. Found, by precipitation as magnesia ammonium phosphate and then as molybdate, 0.0059 g. phosphorus, equivalent to 98.3%.

A compound containing the combined phosphorus could be precipitated from the solution by neutralizing the acid with barium hydroxide and adding two volumes of alcohol. This precipitate, after removal of the barium with sulfuric acid and subsequent precipitation with alcohol, contained 3-5% phosphorus and was later shown to be an organic phosphoric acid. In order that the material could be obtained in sufficient quantities to work with, it was necessary to determine the conditions for its isolation so that it could be carried out on a large scale.

Conditions for Hydrolysis.—As it was necessary to precipitate with alcohol, attempts were made to hydrolyze the starch in as concentrated a solution as possible. A 25% starch solution was found to be the maximum concentration that could be used, since a higher concentration gave too thick a paste. Hydrolysis with strong acid was found to be the best, since dilute acid favors the formation of retrograded starch, a substance that is exceedingly troublesome to filter.

When working with small quantities, it was found possible to evaporate the solution after hydrolysis and subsequent neutralization with ammonia, but when large amounts were used a caramel-like substance was

¹ Anderson, *J. Biol. Chem.*, 20, 487 (1915); Plimmer, *Biochem. J.*, 7, 43 (1913).

formed that was insoluble in alcohol.¹ The formation of this insoluble substance was obviated by allowing hydrolysis and evaporation to take place together. The following conditions were found to be the most satisfactory for this purpose:

Ten kilograms of starch were suspended in forty liters of water and two liters of concentrated hydrochloric acid added. The mixture was stirred and steam under fifty pounds' pressure led in until the stiff paste which first formed had completely liquefied. The solution was then transferred to large evaporating dishes and heated on the water bath at 65° until no precipitate was formed on the addition of a few drops of the solution to alcohol. It was then neutralized by solid barium hydroxide and the solution filtered from the precipitate of retrograded starch, barium phosphate, and barium carbonate, through large fluted papers. The solution, usually twenty to twenty-five liters in volume, was precipitated with two volumes 85% alcohol in large precipitation jars and allowed to settle overnight. As much of the supernatant liquid as possible was then siphoned off and the remainder filtered with suction. About 60 g. of a white hygroscopic substance were obtained in this way from each ten kilograms of starch.

Sixty kilograms of starch were treated by this method, yielding about 300 g. of the barium precipitate. The product was suspended in water and decomposed by a slight excess of sulfuric acid, the solution filtered and the residue extracted three times with water and filtered with suction. The original filtrate and washings were combined and the excess acid removed by long stirring with lead carbonate; the lead carbonate and sulfate filtered off, and the solution made slightly alkaline with ammonia and saturated with hydrogen sulfide to remove the lead. The filtrate from the lead sulfide was evaporated under 25 mm. pressure to a thin syrup and precipitated by the addition of eight liters of glacial acetic acid. By pouring the acid carefully down the side of the precipitation jar and then stirring slowly, a granular precipitate was obtained that could be easily filtered. The precipitate was washed with absolute alcohol and dried in a vacuum desiccator, first over sulfuric acid and then over potassium hydroxide. Yield, 110 g., marked "Acetic acid precipitate." The acetic acid filtrate after evaporation under diminished pressure and subsequent precipitation with alcohol yielded 75 g. of a slightly

¹ Six hundred grams of this substance were obtained in this way from ten kilograms of starch. It contained 0.24% phosphorus and yielded acetyl derivatives containing 0.06-1.59% phosphorus. They could not be sufficiently purified to warrant further investigation. Acid hydrolysis led to the isolation of a substance containing 3.9% phosphorus and similar in properties to those obtained direct from starch. These results suggest the possibility of the formation of phosphorus-bearing polysaccharides from simpler compounds under these conditions.

yellowish powder that contained 3.4% phosphorus. This substance has not been investigated farther.

Acetic Acid Precipitate.—The crude substance when dry was obtained as a dull white, very hygroscopic powder. It was soluble in water, from which solution it could be precipitated by the addition of alcohol, acetone or acetic acid. Upon analysis it gave 4.9% phosphorus, none of which was present as inorganic phosphates. Qualitative analysis of the ash showed the presence of small quantities of magnesia, sulfates, chlorides and silica. It contained no nitrogen and did not reduce Fehling's solution.

Acyl Derivatives.—Owing to the insolubility of the substance in organic solvents, purification was attempted by means of acylation, in the hope that in this way products of definite chemical constitution could be isolated. Acetylation, however, led to the formation of uncrystallizable syrups. This difficulty was avoided by benzoylating the compound by means of the Schotten-Baumann reaction, but the products were colloidal and could not be crystallized, so that purification could only be accomplished by precipitation from chloroform or acetone solution by means of ligroin, ether, water, etc. Two amorphous substances were obtained in this way that were fairly constant in phosphorus content.

Compound "A"..... 1.02, 1.04, 0.99, 1.08, 1.03% phosphorus.

Compound "B"..... 1.48, 1.42, 1.40, 1.41% phosphorus.

Since the products could not be crystallized and gave varying values for phosphorus after more extended treatment it is difficult to say whether or not they were chemical individuals.

Lead Salt.—Purification was then attempted by means of the lead salt, which it was found could be precipitated from alcohol solutions by means of lead acetate. The compound obtained in this way contained constant amounts of lead and phosphorus when prepared under different conditions and appeared to be a definite chemical compound. It was free from inorganic phosphates and from metals other than lead. The results of the analyses of five such preparations with the methods used for their isolation are as follows:

Preparation No.	1.	2.	3.	4.	5.
Per cent. lead.....	30.46	30.30	30.53	30.33	30.38
Per cent. phosphorus.....	3.86	3.80	3.78	3.99	3.90

Method of Preparation.

(1) One gram of the substance was dissolved in 100 cc. of water and precipitated by the addition of 400 cc. of alcohol. The precipitate was then extracted several times with hot 80% alcohol and the combined filtrates precipitated by the addition of lead acetate. A white flocculent precipitate was obtained which was filtered off, dissolved in dilute acetic acid and precipitated with alcohol.

(2) Five grams of the substance were dissolved in 100 cc. of water and a 10% solution of lead nitrate added until no further precipitate was obtained. One hundred cc. of alcohol were then added and the solution allowed to stand in the ice box overnight. The solution was filtered and the filtrate precipitated by the addition of a saturated solution of lead acetate in 80% alcohol. The resulting precipitate was filtered off and reprecipitated from water solution by means of alcohol.

(3), (4) Twenty grams of the substance were dissolved in 200 cc. of water, neutralized with lead carbonate and 9 g. of lead nitrate added. The solution was allowed to stand in the ice box overnight, filtered and the filtrate precipitated by the addition of 400 cc. of alcohol.

(5) Five grams of the substance were dissolved in 50 cc. of water and 10% silver nitrate solution added until no further precipitate was obtained. The silver chloride was filtered off and the excess silver removed by hydrogen sulfide. The hydrogen sulfide was removed by boiling and the solution neutralized with lead carbonate and treated as described under (3).

All preparations were dried for analysis at 60° *in vacuo* over sulfuric acid. Attempts to determine the percentage of carbon and hydrogen were unsatisfactory, owing to the difficulty experienced in burning the substance.

Free Acid.—The free acid was prepared from the lead salt by removing the lead with hydrogen sulfide and precipitating the resultant solution with alcohol, after evaporation of the solution under diminished pressure. The substance contained a constant amount of phosphorus as shown by the following analyses:

Preparation No. ¹	1.	2.	3.	4.	5.	6.
Per cent. phosphorus.....	5.30	5.30	5.56	5.24	5.27	5.33
Carbon ¹	35.45 and 35.20%					
Hydrogen.....	5.84 and 5.93%					

The substance as obtained by the above method was a perfectly white amorphous powder. It was extremely hygroscopic, contained no ash other than phosphoric acid and was free from nitrogen. It reduced Fehling's solution and on hydrolysis with acid yielded a reducing sugar equivalent to 65% glucose, and gave a heavy precipitate of glucosazone.

The substance was optically active. $[\alpha]_D^{22}$ 108° 30'.

Hydrolysis and Identification of the Sugar.—One gram of the material was dissolved in 100 cc. of 10% hydrochloric acid and heated on the water bath for four hours. A large excess of sodium acetate and 2 g. of phenyl hydrazone were then added and the solution heated for two hours longer. A heavy precipitate formed which was recrystallized from methyl alcohol and water containing a small amount of pyridine, and identified as

¹ It was necessary to remove the ash and grind it with potassium dichromate and repeat the combustion in order to burn the substance completely.

glucosazone by means of the melting point and optical rotation. M. p. 204° (uncorr.).

Two-tenths of a gram dissolved in 4 g. of pyridine and 6 g. of absolute alcohol gave a negative rotation¹ in a 25 mm. tube of $27'$.

Quantitative Estimation of the Sugar.—0.3384 g. of the substance was dissolved in 100 cc. of 10% hydrochloric acid and heated on the water bath for eight hours. The solution was then made up to 100 cc. and the sugar determined in two aliquots of 25 cc. each by Defren's method.²

Gram copper oxide.....	0.1417	0.1416
Glucose equivalent.....	0.0630	0.0629
Per cent. glucose.....	64.86	64.81

Probable Constitution of the Compound.

The simplest formula that will conform to the above analyses is $C_{17}H_{41}O_{16}(H_2PO_3)$ corresponding to the calculated percentages; carbon, 35.66; hydrogen, 5.77; phosphorus, 5.42. According to the formula the lead salt contains a higher percentage of lead than should be present (26.73%), were the metal combined only with the phosphoric acid. The percentage of phosphorus in the lead salt calculated on a lead free basis agrees, however, with that found in the free acid. This shows that the excess of lead is not present as an impurity in the form of some other lead salt, since in that case the phosphorus value would have to be less. The excess of lead might be due to the fact that the salt was formed in a strong alcoholic solution, a condition which we know favors the formation of lead salts of the carbohydrates, and that therefore some of the lead might be combined in this way.

The amount of reducing sugar present corresponds to the ratio of one molecule of maltose to one of phosphoric acid (found, 61.70; calc., 59.79). The remainder of the molecule, 26.04%, aside from the phosphoric acid corresponds to the empirical formula $C_6H_{12}O_6$. No evidence for the presence of pentose could be obtained. It was mentioned above that difficulty was encountered in completely burning the sample during combustion owing to the presence of the phosphoric acid. It therefore seems possible that the remainder of the molecule is also a hexose. In view of the fact that it does not reduce Fehling's solution, it might be inositol, or, if another molecule of hexose, be still combined with the phosphoric acid in such a way as to destroy its reducing power. Eight grams of the crude material were examined for inositol, but none could be found, although 60% of the inositol were recovered from phytin treated in a similar way. It is impossible, therefore, to make any definite statement as to the nature of the remainder of the molecule.

NEW YORK, N. Y.

¹ Neuberger, *Ber.*, 32, 3384 (1899).

² Sherman, "Organic Analysis," 1912.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF NEVADA.]

ALFALFA SEED OIL. ALFALFA INVESTIGATION. VI.

By C. A. JACOBSON AND AUGUST HOLMES.

Received November 1, 1915.

In the course of the investigations carried on in this laboratory on alfalfa, the subject of the composition of the oil in the seeds arose, and that led to the following work:

The alfalfa seeds were procured in the local market and were of a good quality. They were ground in a small hand mill so that all were crushed or cracked open, after which the oil contained in them was extracted. The ground seeds previous to extraction yielded the following analysis:

Ash.....	3.43%
Ether extract.....	11.39%
Crude fiber.....	10.52%
Moisture.....	6.35%
Carbohydrates, etc.....	32.43%
Crude protein.....	35.88%
	<hr/>
	100.00%

According to the above analysis about forty pounds of the seeds would be required to yield a sufficient quantity of the oil for the following investigation, and therefore we determined upon a less expensive solvent than ether for the extraction. Gasoline, boiling between 65° and 95°, at 645 mm., pressure was chosen for this purpose. This solvent was found nearly as efficient as ether for the extraction. More precisely, 1.92% less of the oil was extracted by the gasoline than by the ether.

The extraction was carried out in the following manner: The ground seeds were well stirred up with the solvent so that all the particles were wet, and this mash put into long glass tubes. The solvent was then added at the top and allowed to percolate through. In this way the extraction proceeded easily and quickly, the extraction being considered finished when the solvent came through colorless. The gasoline was then distilled off, when the oil passed from the golden yellow color to a chestnut brown. The oil thus obtained was used for the investigation.

The ether extract was yellowish green in color and it is the authors' opinion that the gasoline extract was a purer oil than the ether extract, which must have contained the coloring matter in the seeds as well as the oil.

Properties of the Oil.—The refractive index of alfalfa seed oil is given in the following table:

Temperature.	n.	Temperature.	n.
17°	1.4783	39.9°	1.4695
20°	1.4770	48.9°	1.4664
25.3°	1.4750	59.2°	1.4622
30°	1.4735	69°	1.4587

The oil is a drying oil whose specific gravity was found to be: 0.9117²⁴ and 0.9149²⁴. Its saponification value, 172.3; iodine value, 154.2; acid value, 2.85; acetyl value, 19.8; Reichert-Meissl value, 0.40; unsaponifiable matter, 4.40%; glycerol (by acetin), 1.97%; saponification value of the acetylated oil, 192.2.

Volatile Acids.—To determine whether or not there were any volatile acids in the oil, about 3 g. of the oil were saponified with alcoholic potash, the alcohol evaporated off, an excess of sulfuric acid added and the mixture distilled until the distillate reacted neutral to litmus. The distillate was filtered, thus separating the soluble volatile from the insoluble volatile acids. The two portions were then titrated with decinormal sodium hydroxide solution, with the following results:

G. oil.	Sol. volatile acids, cc. N/10 NaOH.	Insol. volatile acids, cc. N/10 NaOH.
2.944	1.42	0.95
2.910	1.22	1.56

From these results it is concluded that there are practically no volatile fatty acids present in the oil and that there are no lactones present in the free acids.

Insoluble Fatty Acids.—The insoluble fatty acids were prepared by saponifying with alkali, liberating the fatty acids and treating with hot water in the usual manner. The result showed that 92.5% of the oil was in the form of insoluble fatty acids, that is from lauric acid upwards. The acids thus obtained had the following characteristics: neutralization value, 191.5; mean molecular weight, 293; saponification value, 189.9; iodine value, 169.5. The bromide test of *Hehner and Mitchell*¹ yielded 17% of solid bromides.

Unsaturated Fatty Acids.—The free fatty acids were then separated into the liquid and solid acids by the method of *Gusserow-Varrentrapp*,² that is by the lead-salt method. The quantitative experiments carried out on this separation yielded 90.4% of liquid acids and 9.6% of solid acids in the mixture of acids from the oil. The unsaturated acids, thus obtained, had an iodine value of 175.7, while the saturated acids had an iodine value of 8.4.

The unsaturated acids at hand were insufficient for an extended investigation, so a larger quantity was prepared by the method of *Tortelli and Ruggeri* (*L'Orsi* 1900, April) which is claimed to yield unsaturated acids of a greater purity than that of the *Gusserow-Varrentrapp* method. The acids thus prepared gave an iodine value of 187.7, neutralization value 194.4 and a mean molecular weight of 288.6.

To determine the constituents of the unsaturated acids, the method of the formation of the bromides appears to be the simplest, since

¹ *Analyst*, 1898, p. 313.

² *Ann.*, 27, 153 (1828); *Ibid.*, 35, 197 (1840).

Lewkowitsch in both the fourth and fifth editions of his work on Oils, Fats and Waxes, suggests that this may be done. The bromination was carried out in the following manner: About 3 g. of the unsaturated acids were dissolved in 40 cc. ether, to which a little acetic acid had been added, cooled to 5° and then bromine added, drop by drop, until the solution remained a reddish brown. The mixture was then allowed to stand overnight and filtered the next morning, washed with chilled ether, dried in a water oven and weighed. Lewkowitsch¹ recommends to cool to -10°, and this the authors did, but contrary to his statement, a whiter precipitate was obtained by the former method but of a slightly lower melting point (177.2-178.0°). The filtrate was evaporated to free it from ether and digested with low boiling petroleic ether (35-65° at 645 mm.), upon which the residue passed completely into solution but refused to crystallize out, even on standing overnight at approximately zero degrees. The solvent was then evaporated off, the residue dried in the water oven and weighed, yielding the following results:

	G. unsaturated acids.	G. insol. Br derivatives.	% insol. Br derivatives.	Melting point of Br deriv.
Lot 1.....	2.186	0.628	28.7	181.5°
Lot 2.....	2.111	0.608	28.8	180.8-181.6°
	G. unsaturated acids.	G. sol. Br derivatives.	% sol. Br deriv.	
Lot 1.....	2.186	2.746	130.1	
Lot 2.....	2.111	2.980	136.3	
Melting point of linolenic hexabromide.....				180-181

The mean percentage of the insoluble bromine derivatives (28.75) calculated to linolenic acid gives 10.55%, whereas the ether soluble percentage (133.2), calculated as oleic acid, gives 84.85%. Upon the basis that linolenic acid has an iodine value of 274.10, oleic acid 90.07 and linolic acid 181.42, the iodine value of the mixed unsaturated acids should be 105.34, whereas that found was 187.7. Evidently from this, and especially since the same results were obtained in four different experiments and two different samples of unsaturated acids, the bromine derivatives are only good to estimate the linolenic acid, the remaining unsaturated acids being unadapted to the method.

To determine the other acid or acids, recourse was had to the alkaline permanganate oxidation. This was carried out according to Hazura.² The weight of the water-soluble hydroxy acid was 2.9 on a 30 g. sample; the water-insoluble, 21 g. The water-soluble was crystallized from alcohol and water, yielding a pure white product which melted at 173.8°, and had a neutralization value of 147.7. This corresponds to isolinusic acid which melts at 173-175° (Hazura), and has a neutralization value of

¹ 5th Ed., Vol. I, p. 573.

² *Monatsh.*, 1887, 260, *et seq.*

147.6. A previous oxidation of the unsaturated acids was carried out by passing sulfur dioxide gas into the solution, in place of adding sulfurous acid, yielding an acid melting at 196–198° which signifies the normal linusic acid. Thus both the linusic and isolinusic acid can be obtained from the same unsaturated acid, since in the latter case, no linusic was formed, but in the former, linusic acid was the chief product.

The water-insoluble hydroxy acids were extracted with ether, thus giving the ether soluble and ether insoluble acids. 5.3 g. or about 18% of the oil was unoxidized and remained in the ether solution after the hydroxy acids crystallized out upon the evaporation of the solvent. These latter hydroxy acids (0.41 g.), after being crystallized from alcohol melted at 131.2–131.4° and had a neutralization value of 177.7. This corresponds to dihydroxy-stearic acid, whose melting point and neutralization value LeSueur¹ finds to be 131.5–132.0° and 177.6, respectively.

The ether insoluble portion (9.04 g.) was first fractionated by exhausting with 30% alcohol as recommended by Meyer and Eckert² with the following results:

Fraction.	Melting point.
1.....	156–7°
2.....	167.6–168.0°
3.....	173.6–173.8°

Fraction 3, indicates sativic acid since Hazura gives 173° and Hehner and Mitchell 174° as its melting point. Nevertheless, Fraction 3 was again exhausted with water, yielding four fractions with the following melting points: 1st, 173.4–174.2°; 2nd, 177.2°; 3rd, 177.8°; and 4th, 177.6°. The third and fourth fractions were combined and yielded a neutralization value of 161.0 (theoretical for sativic acid 161.2). This is the highest melting point yet recorded for sativic acid, although Hartley³ obtained 175° and Thoms⁴ 177° as the melting point of sativic acid obtained from telfairic acid. This increase in the melting point raised the suspicion that the other fractions (*i. e.*, 1 and 2) must contain another acid, and so they were exhausted with boiling water, with the following results: Fraction 2 yielded five subfractions of different melting points, namely: 1st, 160.6° and neutralization value 159.6; 2nd, 166.4°; 3rd, 171.4°; 4th, 174.6°; 5th, 176.0°. As can be seen, the neutralization value speaks of no second acid present, so the acid must be isomeric with that found in Fraction 1. This is shown to be true by exhausting Fraction 1 with boiling water, yielding the following results:

¹ *J. Soc. Chem. Ind.*, 1900, 845.

² *Monatsh.*, 31, 1243 (1910).

³ *J. Physiol.*, 38, 367 (1909).

⁴ *Z. angew. Chem.*, 1904, 1483.

Fraction.....	1	2	3	4	5	6
M. p.....	158.2	158.0	158.3	158.3	159.2	159.4
Fraction.....		7	8	9	10	11
M. p.....		158.6	158.4	159.2	158.7	159.1

Fractions 1, 2, 3 and 4 were combined and gave a neutralization value of 159.3, Fractions 5 and 6 combined gave 160.7 and Fractions 7, 8, 9, 10 and 11 combined gave a neutralization value of 159.3. In addition, a determination of carbon and hydrogen on the first four fractions mixed, gave 62.08% C and 10.06% H. Theoretical for tetrahydroxystearic acid: 62.02% C and 10.42% H.

Thus, in the first fraction from the oxidation products of alfalfa seed oil, there seem to be two, and possibly three different tetrahydroxy acids present with almost the same melting points (158.2° , 159.4° and 158.8°), but with considerably different solubilities in water, the first fractions yielding granular and amorphous powders while the last are silky crystals.

The oxidation products have therefore revealed the presence, in alfalfa seed oil, of oleic, linoleic and linolenic acids in the proportion of 3.3, 73.2 and 23.5%, respectively, but calculating from the bromine derivatives and the iodine value, they are present to the extent of 3.94, 85.51 and 10.55%, respectively. The former values are considered the more trustworthy.

Saturated Fatty Acids.—The solid saturated fatty acids were obtained by the lead salt separation of the mixed fatty acids, and were purified to a perfectly white mixture by crystallization of the acids from alcohol and the judicious addition of water. After trying several proposed methods for the separation of the saturated acids, the fractional crystallization from alcohol was the method adopted as being the most accurate and expeditious.

The saturated acids gave a neutralization value of 207.7 and a mean molecular weight of 270.2. The melting point was 51.2° and solidifying point 48.8° . About 9.6 g. of the saturated acids were taken and crystallized from 100 cc. absolute alcohol. The first fraction of the crystallized acids had a melting point of 65.8 – 66.2° , and a neutralization value of 151.0. This fraction was recrystallized three times, the last two subfractions melting at 81.2 – 81.5° and 83.8° , respectively. The acids from Fraction 1 were then liberated from their potassium soaps by hydrochloric acid, washed and crystallized from 90% alcohol. The first subfraction of this crystallization melted at 74.2° and the second subfraction at 73.8 – 74.0° .

Judging from the previously obtained neutralization value, either carnaubic or lignoceric acids were present. The melting point of carnaubic acid is 74° according to Meyer and Eckert,¹ but 72.5° according

¹ *Monatsh.*, 31, 1233 (1910).

to Stürcke.¹ Dunham and Jacobson² found carnaubic acid to melt at $72.0-72.5^{\circ}$. Since lignoceric acid melts at 80.5° , carnaubic acid ($C_{24}H_{48}O_2$) must be the one present in alfalfa seed oil.

From the two sets of melting points of carnaubic acid, obtained by different investigators, it would appear that this acid exists in two metameric forms. The high melting points obtained upon Subfraction 1 and 2, from this fraction, would indicate the presence of behenic acid ($C_{22}H_{44}O_2$), but not enough material was at hand to establish this point.

The crystallization was carried further by cooling the solution and the final fractions obtained by the addition of small quantities of water until ten fractions in all were separated. Fractions 9 and 10 melted at 59.6° and 59.2° , respectively. Fraction 9 had a neutralization value of 207.5. The last five fractions were combined and again fractionally crystallized from 70% alcohol, yielding four subfractions melting, in order, at 56.6° , 58.0° , 59.6° and 56.6° , the last being obtained by the addition of a large quantity of water. The first fraction melting at 56.5° was again fractionally crystallized, yielding three subfractions melting from 57.2° to 59.8° . The fraction melting at 57.2 was again recrystallized from alcohol by adding water without change in melting point. It had a neutralization value of 207.5.

From this it is concluded that an acid having a melting point of $59.6-59.8^{\circ}$ and a neutralization value of 207.5 is present in the acids from alfalfa seed oil. This corresponds to daturic acid ($C_{17}H_{34}O_2$), obtained by Meyer and Beer³ from datura oil with a melting point of 59.5° and a neutralization value of 207.6, and is the same as Krafft's synthetic margaric acid. In this connection it is interesting to note that Meyer and Eckert⁴ obtained an acid of the same formula as daturic, from coffee-berry oil, having a melting point of 57° , which, when taken in connection with the above results, points to the existence of two metameric forms of daturic acid.

Conclusion.

Alfalfa seed oil is a drying oil whose physical properties resemble safflower oil. It contains practically no volatile acids but 92.5% of the oil is composed of insoluble fatty acids. The fatty acids in the oil contain 90.4% liquid acids and 9.6% solid acids. The liquid acids are composed of oleic, linoleic and linolenic acids, and the solid acids of carnaubic, daturic and possibly behenic acids.

The above investigation was carried out at The Nevada Agricultural Experiment Station with funds obtained under the Adams Act.

RENO, NEVADA.

¹ *Ann.*, 223, 306 (1884).

² *Z. physiol. Chem.*, 64, 307 (1910).

³ *Kaiserl. Akad. d. Wissenschaften*. Wien, Jan., 1912.

⁴ *Loc. cit.*

NOTE.

On the Stability of Silver Fulminate under Water.—While looking over some old material recently, the writer found a small specimen of silver fulminate which had been prepared many years ago by the late Dr. Robert Peter, then Morrison Professor of Chemistry and Physics in Kentucky University, and used by him for illustration in connection with his lectures. These lectures were delivered in the chemical lecture room of Morrison College, where the writer distinctly remembers seeing this specimen when, as a student, he attended them in the seventies. Inasmuch as Dr. Robert Peter ceased lecturing in this room in 1878, having removed to another building, it follows that the specimen must be at least thirty-seven years old and it is probably several years older.

The material is distinctly crystalline, but is of a mouse-gray color, as the result of long exposure to the light. It is contained, under water, in a small glass stoppered bottle, the stopper being well greased. The water is colored somewhat brownish, probably from the grease on the stopper, but is neutral to litmus paper. The fulminate, after drying, was found to detonate strongly when struck or when heated, and also when touched with concentrated sulfuric acid. Addition of dilute HCl caused a rapid decomposition with production of a voluminous precipitate of AgCl and a smell like that of HCN (Nef's formyl chlorid oxide).

A determination of silver was made by drying a portion in a porcelain dish, in a desiccator, at room temperature, decomposing it by evaporating with dilute hydrochloric to which a little nitric acid had been added, and heating the resulting silver chlorid to incipient fusion before weighing. By this process 0.1171 g. of the material gave 0.1118 g. AgCl.

Calc. for CNOAg: 71.97%. Found: 71.86%.

For comparison, two recently prepared specimens of silver fulminate were treated in the same way, giving the following results, respectively: 0.0918 g. silver fulminate gave 0.0880 g. AgCl, and 0.3055 g. silver fulminate gave 0.2922 g. AgCl.

Calc. for CNOAg: 71.97%. Found: 72.03 and 71.98%,

showing that this method gives good results and that the old specimen had the same composition as the fresh specimens.

It is interesting to note that silver fulminate does not undergo decomposition under water and under ordinary laboratory conditions during the lapse of so long a time.

ALFRED M. PETER.

NEW BOOKS.

A Practical Elementary Chemistry. By B. W. McFARLAND, High School, New Haven, Conn. 462 pp., 148 cuts. Scribners.

This book is different. Most first year textbooks are written and afterward a laboratory manual is arranged which follows more or less closely the text, the manual either separate or bound in with the text. This book puts the manual first, filling 100 pages and giving 47 experiments, though many of these are too long for one laboratory period. This is followed by Part II, Fundamental Ideas, pages 104 to 165; Part III, Advanced Theory, pages 168-238; and Part IV, Descriptive, pages 251 to 454. The Index fills 8 pages.

Such an arrangement should free the teacher from slavery to a text and is pedagogically right in basing the study on laboratory work, not on a textbook. It is an extension of the plan followed by two well-known and formerly widely used books, Remsen, and Shepard. In these the directions for laboratory work are printed in different type in the body of the text. Whether the entire separation of the two parts as given here is practically advantageous remains to be seen. The author is quite complacent over the results obtained while using it. They may be due to the teacher rather than to the plan.

Each chapter of the first three parts is followed by exercises, questions and problems designed to provoke thought, though in some cases the student is told what he should have discovered. *E. g.*, page 59: "Note that the odor has been removed." "Note that the color has been removed." "Note that the bitter taste has been removed." The references are all to paragraphs but none of these are given at top of page and much time must be spent looking through the work to find the required paragraph.

Aside from the features enumerated the book has no distinctive differences. The subject of equations receives much attention and Chapter XIX is made up entirely of review exercises. Carbon and its compounds get ten pages of descriptive text and the metals 76, of which 17 are given to the alkalis. Five pages go to Osmosis and related topics, 10 to Electrochemistry and 3 to Thermochemistry. Gram molecular volume is given but the Kinetic molecular hypothesis is not mentioned.

The terminology leaves much to be desired. Sugar dissolves in water and copper dissolves in nitric acid, as though the two were the same; there is "suction" and precipitates are "sucked dry," as though his students would not understand unbalanced atmospheric pressure; there are hydrogens and oxygens and bariums and aluminums and 2 KBr's (two kay bee ar's or two potassium bromides?); logically there should be sodiums, or would they be sodas? and coppers might be shortened to "Cops." Such usage might, perhaps, be permissible elsewhere. It has no place in a text for beginners. " $\text{N}_2\text{O} + \text{H}_2\text{O} = 2\text{HNO}$ " and the statement "NO

is the hyponitrite radical and has a valence of one because it can form a compound with one hydrogen" are surprising to say the least and the word "symbol" is given four distinct meanings. "Chemistry teaches us the value of 40 or more elements or compounds" and "Valence is taught only to relieve the student of the necessity of remembering the combining proportions of the elements in thousands of compounds," need reconciling.

The type, illustrations and presswork are good. A few misprints such as the last formula on p. 135, "pyrophoric" on p. 148 and carbon dioxide, p. 332, escaped the proofreader.

In spite of all these the book will well repay a reading and will appeal to those desiring a change in plan. C. M. WIRICK.

The Analysis of Non-Ferrous Alloys. By FRED IBBOTSON, B.Sc., B.MET., A.R.Sc.I. AND LESLIE AITCHISON, M.MET. With diagrams. London, New York: 1915. Longmans, Green & Co. pp. vii + 230.

The aim of this volume is to assemble the methods which, in the opinion of the authors, combine accuracy and speed in the highest degree, and apply to conditions which are actually to be met with in analytical practice. The various metals treated in the volume are first considered from the viewpoint of pure solutions, and subsequently as constituents of alloys.

The subject matter is divided into fifteen chapters, the first of which treats of apparatus used for electrolytic analysis, the second with the underlying principles of electrolytic analyses, the third with precipitations by means of hydrogen sulphide, the last with the analysis of commercial alloys, and the others with the determination of the various elements found in non-ferrous alloys. There is an appendix containing directions for the preparation of certain reagents, and the preparation of platinum electrodes. Five-place logarithms are also included. The index is subdivided into author and subject indexes.

The book is noteworthy as an assemblage of data which are widely distributed in journal literature, and as a contribution to a field which is not efficiently covered, but is of growing importance. The book is not without some rather serious imperfections in composition and directness of statements but, in spite of these imperfections, the authors have made a distinct contribution to analytical chemistry. H. P. TALBOT.

THE JOURNAL

OF THE

American Chemical Society

with which has been incorporated the

American Chemical Journal
(Founded by Ira Remsen)

TWENTY-THIRD ANNUAL REPORT OF COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED DURING 1915.

By GREGORY PAUL BAXTER.

Received January 26, 1916.

The number of new researches upon the atomic weights published during the past year is as large as could be expected under prevailing conditions.

For the first time since 1912 the International Committee on Atomic Weights¹ recommends changes in the accepted values for a few elements. These changes are as follows:

	1912.	1916.
Carbon.....	12.00	12.005
Sulfur.. ..	32.07	32.06
Helium.....	3.99	4.00
Tin.....	119.0	118.7
Lead.....	207.10	207.20
Radium.....	226.4	226.0
Uranium.....	238.5	238.2
Ytterbium.....	172.0	173.5
Praseodymium.....	140.6	140.9
Yttrium.....	89.0	88.7
Lutecium.....	174.0	175.0

Oxygen.—Germann² discusses critically determinations of the density

¹ THIS JOURNAL, 37, 2449 (1915).

² *J. Phys. Chem.*, 19, 437 (1915).

of oxygen and describes in detail his own experiments in this field.¹ His final conclusion is that the weight of the normal liter is 1.42905 g.

Carbon.—By analysis of the calcium and ammonium salts of salicylic acid and the ammonium salts of *m*- and *p*-oxybenzoic acids Oechsner de Coninck² found the molecular weight of these acids to be 137.99. If H = 1.008, carbon is 11.99. As only four experiments were performed and the quantities used were very small, this result has little significance.

Copper.—Shrimpton³ compared the weights of simultaneous silver and copper deposits. The silver cells were of the Guthe-Richards porous pot type. Corrections were made for inclusions in the silver and for cathodic solution of the copper. Vacuum weights are given.

Weight Ag.	Weight Cu.	At. wt. Cu.	Weight Ag.	Weight Cu.	At. wt. Cu.
2.21697	0.65306	63.567	2.29785	0.67673	63.572
2.21636	0.65309		2.29783	0.67724	
	0.65305			0.67701	
	1.27358	63.561		0.67718	(63.558)
4.32294	1.27341		3.54120	1.04372	
4.32294	1.27351		3.54370	1.04339	
	1.27346	63.563		1.04367	63.562
	0.64406			1.04327	
2.18669	0.64406		3.91789	1.15430	63.562
2.18601	0.64416	63.559	3.91852	1.15434	
	0.64407			1.15362	
	0.64415	63.559		1.15486	(63.556)
	0.63264		4.83364	1.42323	
2.14755	0.63262		4.82973	1.42331	63.562
2.14747	0.63255	63.561		1.42331	
	0.63266			1.42320	
	0.95570	63.561		0.71818	63.562
3.24431	0.95580		2.43820	0.71844	
(3.24523)	0.95581		2.43837	0.71828	
	0.95564			0.71835	
Average,					63.563

Molybdenum.—Müller⁴ has determined the atomic weight of this element by oxidizing weighed amounts of the metal in a current of air and weighing the resulting oxide. The metal was prepared by reduction in hydrogen from oxide which had been fractionally sublimed as hydroxychloride in a current of hydrochloric acid. Quartz apparatus was utilized. Weights are corrected to vacuum.

¹ *Comp. rend.*, 157, 926 (1913); see also 21st Annual Report, *THIS JOURNAL*, 36, 457 (1914).

² *Compt. rend.*, 160, 67 (1915):

³ *Proc. Phys. Soc. London*, 26, 292 (1914).

⁴ *THIS JOURNAL*, 37, 2046 (1915).

Fraction.	Weight Mo.	Weight MoO ₃ .	At. Wt. Mo.
I.....	0.52591	0.78879	96.027
I.....	0.56327	0.84487	96.012
I.....	1.12757	1.69117	96.031
II.....	0.53014	0.79517	96.014
II.....	1.10754	1.66130	96.002
II.....	1.62166	2.43181	96.080
II.....	1.45530	2.18259	96.047
III.....	0.94968	1.42428	96.048
III.....	0.65659	0.9870	96.054

Mean, 96.035
Mean, omitting the 6th analysis, 96.029

Cadmium.—Oechsner de Coninck and Gérard¹ ignited weighed amounts of cadmium carbonate and then reduced the resulting oxide to metal in a current of hydrogen. It is worth noting that an error of 0.1 mg. in the weight of the metal would alter the atomic weight by nearly one-tenth of a unit.

Weight CdCO ₃ .	Weight Cd.	At. wt. Cd.
0.5500	0.3585	112.32
0.6050	0.3943	112.28
0.6600	0.4302	112.32
0.6171	0.4023	112.37
0.5445	0.3549	112.31

Average, 112.32

Cadmium.—Hulett and Quinn² have published a paper in support of their earlier work.

Tin.—Briscoe³ purified stannic chloride by fractional distillation, the portions analyzed being collected in weighed bulbs. After being re-weighed the bulbs were broken under a solution of oxalic and nitric acids and the chloride was compared with weighed amounts of pure silver. Vacuum weights are given.

Cl = 35.460.

Weight SnCl ₄ .	Weight Ag.	At. wt. Sn.	Weight SnCl ₄ .	Weight Ag.	At. wt. Sn.
9.02435	14.9475	118.685	7.55785	12.5183	118.688
9.39855	15.5666	118.696	9.11535	15.0983	118.683
10.32760	17.1058	118.689	9.22875	15.2866	118.675
9.17005	15.1880	118.699	9.21890	15.2696	118.686
6.68995	11.0808	118.686	11.29055	18.7017	118.675
9.33130	15.4570	118.666	9.89635	16.3912	118.694
7.77450	12.8764	118.702	9.43385	15.6250	118.696
9.22730	15.2840	118.678			

Average, 118.686

¹ *Compt. rend.*, 161, 676 (1915).

² *THIS JOURNAL*, 37, 1997 (1915).

³ *J. Chem. Soc.*, 107, 63 (1915).

Praseodymium.—Baxter and Stewart¹ purified praseodymium material by fractional crystallization of the double ammonium nitrate. Each fraction was converted to chloride, which, after fusion in an atmosphere of hydrochloric acid gas, was compared with silver and silver chloride in the usual way. Weights are corrected to vacuum.

Cl = 35.457.

Fraction.	Weight of PrCl ₃ .	Weight of AgCl.	At. wt. Pr.	Weight of Ag.	At. wt. Pr.
3474	4.12848	7.17915	140.913
3474	6.91605	12.02533	140.939
3474	7.66554	13.32931	140.923	10.03129	140.943
3474	5.01155	8.71379	140.941	6.55898	140.914
3474	8.78959	11.50311	140.924
4383	6.04235	10.50744	140.909	7.90820	140.910
4383	6.14745	10.69050	140.902	8.04563	140.914
4381	6.32550	10.99855	140.937	8.27886	140.908
4381	5.12982	6.71359	140.920
4381	4.59463	7.98940	140.925	6.01331	140.915
4381	4.77556	6.24994	140.921
4379	5.96661	10.37554	140.913	7.80908	140.910
4379	6.87536	11.95508	140.928	8.99824	140.915
4377	5.73602	7.50707	140.917
4377	4.64585	8.07758	140.951	6.08029	140.917
4374	6.85492	11.91774	140.965	8.97148	140.916
4374	8.01711	13.93953	140.943	10.49250	140.916
4374	6.17045	10.72833	140.952	8.07425	140.959
4374	6.90040	11.99946	140.911	9.03064	140.926
4374	7.08498	12.32019	140.916	9.27274	140.911
4374	5.81310	7.60811	140.911
4371	6.20845	10.79552	140.926	8.12541	140.915
4371	7.07590	12.30401	140.924	9.26045	140.922
4368	5.77646	10.04403	140.935	7.56000	140.916
4368	5.72002	9.94651	140.919	7.48596	140.922
Average, 140.932				140.919	

A very small proportion of cerium in Fractions 4368 and 4371 was quantitatively determined. When a correction is applied for this impurity, the average result of all the experiments is 140.924.

Tantalum.—Sears and Balke² have investigated the ratio, TaCl₅ : 5Ag. The chloride was prepared from the oxide by distillation in a current of sulfur monochloride and the product was fractionally distilled. In Series I the chloride was hydrolyzed in a current of moist air, and the hydrochloric acid was absorbed and compared with silver. In Series II the chloride was transferred to a stoppered platinum weighing bottle without exposure to moisture, and after being weighed it was dissolved

¹ *Proc. Nat. Acad.*, 1, 77 (1915); *Proc. Am. Acad.*, 50, 171 (1915); *THIS JOURNAL*, 37, 516 (1915); *Z. anorg. Chem.*, 92, 171 (1915).

² *THIS JOURNAL*, 37, 833 (1915).

in a large platinum flask in hydrofluoric acid solution concentrated enough to prevent the precipitation of silver tantalate. The chloride was next compared with silver. In Series III the same method of analysis was used, but the number of distillations to which the chloride was subjected varied. Vacuum weights are given in the following tables:

SERIES I.

Weight of TaCl ₅ .	Weight of Ag.	At. wt. Ta.
11.66795	17.51344	182.06
7.61398	11.42585	182.14
4.09519	6.15647	181.50
8.09039	12.16628	181.40

SERIES II.

Weight of TaCl ₅ .	Weight of Ag.	At. wt. Ta.
3.53605	5.31834	181.34
2.99083	4.49851	181.32
6.21118	9.34345	181.27

SERIES III.

Weight of TaCl ₅ .	Weight of Ag.	At. wt. Ta.
4.03892	6.07417	181.36
3.32164	5.00133	180.96
2.68304	4.04002	180.93
3.01453	4.53953	180.90
3.95846	5.95931	181.00

The research is avowedly preliminary. The authors believe the composition of the chloride to vary with the conditions of distillation and are at present investigating this matter.

Lead.—Nonradioactive lead has been investigated by Baxter and Thorvaldson¹ and Baxter and Grover.² The first named compared lead bromide, which had been fused in an atmosphere containing hydrobromic acid, with silver and silver bromide. Br = 79.916. Weights are corrected to vacuum.

Weight of PbBr ₂ .	Weight of Ag.	At. wt. Pb.	Weight of AgBr.	At. wt. Pb.
6.55858	3.85610	207.14	6.71241	207.15
4.83285	2.84126	207.17
5.67758	3.33787	207.17
6.73361	3.95874	207.16	6.89124	207.17
5.93130	3.48660	207.21
5.01729	2.94968	207.17	5.13400	207.22
5.89902	3.46730	207.25
7.71526	4.53498	207.24	7.89526	207.20
7.40244	4.35157	207.20
7.01144	4.12154	207.21	7.17470	207.21
6.91460	4.06484	207.19	7.07672	207.16
8.12623	4.77679	207.22		

Average, 207.19

Average, 207.19

In a similar series of experiments Baxter and Grover corrected for a trace of insoluble material in the fused lead bromide, which is neglected in the above series. The outcome of the two series is essentially the same.

¹ THIS JOURNAL, 37, 1020 (1915).

² Proc. Nat. Acad., 1, 71 (1915); THIS JOURNAL, 37, 1027 (1915).

Weight of PbBr.	Weight of Ag.	At. wt. Pb.	Weight of AgBr.	At. wt. Pb.
5.27845	3.10271	207.23
2.65094	1.55822	207.23
4.08449	2.40104	207.17
4.97508	2.92473	207.15
4.05573	2.38398	207.20	4.15017	207.18
3.44158	2.02288	207.23	3.52224	207.14
5.17416	3.04158	207.19	5.29498	207.17
3.84522	2.26022	207.21	3.93446	207.22
4.30542	2.53086	207.19	4.40616	207.15
4.53467	2.66549	207.21	4.64048	207.18
5.78467	3.40044	207.19	5.91976	207.17
4.87104	2.86337	207.19	4.98467	207.18
6.28465	3.69447	207.19	6.43124	207.19
4.74644	2.79011	207.21	4.85708	207.20
6.82444	4.01148	207.21	6.98380	207.18
6.53721	3.84274	207.20
4.10128	2.41088	207.18	4.19791	(207.09)
2.64271	1.55352	207.18
6.30717	3.70718	207.23

Average, 207.20

Average, 207.18

In order to determine whether common lead always possesses the same atomic weight Baxter and Grover also analyzed lead chloride which had been prepared from minerals from known widely different geographical sources. None of the material was radioactive.

Cl = 35.457.

Mineral.	Source.	Weight of PbCl ₂ .	Weight of Ag.	At. wt. Pb.	Weight of AgCl.	At. wt. Pb.
		5.63567	4.37200	207.21
	Commercial	5.58730	4.33427	207.22
	nitrate	6.86319	5.32402	207.22
Galena	Joplin, Mo.,	4.70770	3.65223	207.20
	U. S. A.	4.20222	3.25968	207.23
Cerussite	Wallace, Id.,	7.04688	5.46691	207.20
	U. S. A.	5.88935	4.56868	207.22
		6.96370	7.17754	207.22
		6.89046	7.10231	207.21
Vanadinite and wulfenite	Tucson, Ariz.,	4.90083	3.80171	207.22
	U. S. A.	5.79300	4.49404	207.21
Galena	Metalline Falls,	5.43965	4.21992	207.21
	Wash., U. S. A.	5.74504	4.45674	207.22
Galena	Nassau, Germany	6.57216	5.09849	207.21
		5.66330	4.39340	207.21
Cerussite	Eifel Mts., Ger-	5.73434	4.44857	207.21
	many	4.17445	3.23862	207.19
Cerussite	New South Wales	6.25884	4.85584	207.19
		5.25882	4.07933	207.23
		7.33227	7.55732	207.22
		6.51699	6.71690	207.23
		Average, 207.21				207.22

The average of all the different series of results is 207.20. This value is perceptibly higher than that obtained some years ago by Baxter and Wilson.

Radioactive Lead.—Hönigschmid and Mme. St. Horovitz¹ have continued their investigation upon radioactive lead by analysis of lead chloride prepared from carefully selected minerals.

Source.	Weight of PbCl ₂ .	Weight of Ag.	At. wt. Pb.	Weight of AgCl.	At. wt. Pb.
St. Joachimsthal, Pitchblende.....	2.91224	3.01042	206.410
	2.47886	2.56256	206.396
	2.76797	2.86126	206.413
	Average, 206.405				
Crystallized uranium oxide, Morogoro, German East Africa.....	3.24177	2.52563	206.024	3.35537	206.054
	3.94867	3.07636	206.025	4.08686	206.066
	3.78263	2.94693	206.033	3.91519	206.053
	3.68899	2.87400	206.030	3.81830	206.052
	4.49731	3.50343	206.054	4.65464	206.070
	Average, 206.033		Average, 206.059		
Bröggerit, Moos, Norway.....	4.50069	4.65794	206.082
	4.49363	4.65060	206.084
	Average, 206.083				
Bröggerit, Moos, Norway, distilled PbCl ₂	4.83605	3.76724	206.060	5.00512	206.076
	3.97826	3.09903	206.060	4.11741	206.072
	4.91204	3.82647	206.057	5.08425	206.050
	Average, 206.059		Average, 206.066		
Common lead, distilled PbCl ₂	6.17861	4.79374	207.177	6.36895	207.193
	4.75170	3.68659	207.182	4.89837	207.176
	4.83397	3.75047	207.178	4.98328	207.170
	Average, 207.179		Average, 207.180		

The leads from Morogoro and Moos possess a lower atomic weight than any other specimen of radioactive lead which has been examined.

Guye and Germann² have calculated the effect on various atomic weights of the gaseous impurities which they have found in silver.³ Inasmuch as their investigations were not carried out with silver prepared with the care necessary for atomic weight experiments, it is premature to rely upon the corrections which they compute.

¹ *Sitzb. k. Akad., Wien, Abt. IIA*, 123, 1 (1914); *Monatsh.*, 36, 355 (1915).

² *Compt. rend.*, 159, 992 (1914).

³ See Twenty-second Annual Report; also *Compt. rend.*, 159, 225 (1914).

The idiosyncrasies of the silver coulometer have been further investigated by Richards and Anderegg,¹ and Hulett and Vinal.²

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS, PUBLISHED BY PERMISSION OF THE DIRECTOR.]

INCLUSIONS IN THE SILVER VOLTAMETER DEPOSITS.

By G. W. VINAL AND WM. M. BOVARD.

Received December 31, 1915.

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1. Introduction.

In a previous paper³ on the voltameter a brief discussion of the question of inclusions of foreign materials in the silver voltameter deposits was given, together with a short résumé of other papers on this subject and a few experiments which had been made at the Bureau of Standards. It was pointed out that, in so far as the international ampere is concerned, the value assigned to the electrochemical equivalent of silver by the London Conference has been generally accepted by the various National laboratories as applying to the silver as we find it deposited in the voltameter, without reference to any inclusions that it may contain. This is not a serious matter because the uniformity of the results obtained by the National laboratories working together, indicated that the inclusions must be very small or very constant in amount and the International committee was enabled to fix the voltage for the Weston normal cell with sufficient accuracy for present purposes. But it was also stated in the reference mentioned above that it is important, if possible, to eliminate any error due to the inclusions, in order that we may know what deviation there is, if any, from the value assigned to the electrochemical equivalent of silver (1.11800 mg. per coulomb).

The earliest experiments of the Bureau on the inclusions in the silver were few in number and were not considered conclusive. Only one deposit was heated to incandescence and that was from an electrolyte in

¹ THIS JOURNAL, 37, 675 (1915).

² J. Phys. Chem., 19, 173 (1915).

³ "The Silver Voltameter," Part IV, by Rosa, Vinal, and McDaniel, *Bull. Bur. Standards*, 10, 516, reprint No. 220.

which impurities were purposely introduced. Its result had, therefore, no significance so far as the value derived for the Weston normal cell was concerned, since only pure electrolytes were used for that purpose.

We have now carried out at the Bureau some further experiments, principally to determine the loss of weight of the deposits when heating them to temperatures of 600° or more. These will be recorded in the present paper, and also a few experiments bearing on the question of the anode liquid.

Richards and Anderegg¹ have recently made determinations of the inclusions of foreign material in the silver deposits. They found the inclusions in their deposits to be very variable and large enough to be a serious source of error in the silver voltameter determinations. They recommended as a safe and convenient method for determining these inclusions that the platinum cups containing deposits should be heated to dull redness in a flame and reweighed.² The resulting loss in weight they attributed to the expulsion of foreign material in the deposit. We have repeated this part of their work and we have extended the experiments to include comparisons with the effect when similar deposits are heated in an electric furnace. Van Dijk³ has previously used a furnace for this purpose. Our furnace was considerably larger than his, so that we could heat our regular platinum cathodes in it.

We found the losses on glowing the deposits to be only 0.004% on the average and fairly constant. We also found that both these methods of heating the deposits are subject to a source of error. In order to drive the inclusions out of the deposited silver a temperature of about 600° has been used and there is necessarily more or less alloying of the silver with the platinum cup. On removing this silver there is left behind a stain of platinum black. This may be so slight as to be hardly noticeable, but if deposits are made without entirely removing the stains the deposited silver does not accurately represent the quantity of electricity that has passed through the voltameter and if such a deposit is heated to dull redness the observed loss in weight depends more on the loss of adsorbed material from the platinum black than on the expulsion of inclusions from the deposited silver. This source of error was not mentioned by previous observers.

2. Apparatus Employed.

(a) The Electric Furnace was designed and built by Prof. G. A. Hulett for this work and we are greatly indebted to him for the use of it. It

¹ THIS JOURNAL, 37, 15 (1915).

² Essentially the same method has been previously described and used by Lord Rayleigh and Mrs. Sedgwick, *Phil. Trans.*, 175, 430 (1884); Jaeger and von Steinwehr, *Z. Instrumentenk.*, 28, 354 (1908); Boltzmann, *Sitzb. Akad. Wiss., Wien, IIA*, 121, 1060 (1912).

³ *Ann. Physik*, 19, 263 (1906).

was constructed from a glazed porcelain beaker and the heating coils of nichrome wire were wound not only on the sides and bottom, but there was also a heating coil in the porcelain cover in order to provide as uniform a temperature inside as possible. Temperature measurements were always made by a platinum-platinum-rhodium thermocouple which had been calibrated at this Bureau. The thermocouple passed into the furnace through a porcelain tube in the center of the cover. The outside of the furnace consisted of two concentric hollow cylinders of metal and asbestos. The double air space thus provided gave ample heat insulation to make the furnace efficient for temperatures not exceeding 750° . The top of the furnace was of glazed porcelain rings, one of which supported the interior parts. The outside dimensions of the furnace are 21 cm. diameter by 27 cm. high, and the inside dimensions are 9 cm. diameter by 16 cm.

The platinum cups, one at a time, were lowered into the furnace with platinum-tipped tongs and rested on a network of platinum wires woven in a perforated porcelain plate. The cups were covered with glazed porcelain crucible tops to prevent the accidental falling of any particles into them when putting the thermocouple in place. The electric current was applied gradually by steps of one ampere at intervals of a few minutes until the maximum current of 7.7 amperes was reached. After each heating the furnace was allowed to cool to about 300° before opening it.

The furnace was designed with a view of avoiding the difficulties of metal contamination sometimes encountered with platinum wound furnaces.¹ To test this an empty platinum cup was heated four times and weighed after each heating with the results given in Table I.

TABLE I.			
Date. 1915.	Wt. of cup. G.	Δ . Mg.	Treatment of cups.
July 23.....	38.496887	-0.019	Washed and dried 160°
	942	+0.036	Heated to 650°
	897	-0.009	Heated to 648°
24.....	897	-0.009	Heated to 646°
<hr/>			
	Mean, 38.496906	± 0.018	

Each of the four determinations given in Table I is subject to the same experimental error in so far as the weighings are concerned. Since the deviations are by small amounts the results show that the heating to a high temperature was without effect on the weight of the cup.

(b) **For Heating by the Flame Method**, the platinum cups were supported on a quartz triangle and covered with a small glazed porcelain evaporating dish. The room was darkened and the cup heated quickly and as uniformly as possible to a very dull red with a Bunsen burner held

¹ *Proc. Am. Acad. Sci.*, 38, 460 (1903).

in the hand. We made a number of determinations on empty platinum cups to determine the effect of heating. The following results, Table II, give the weight after each heating to about 600°:

TABLE II.

Date. 1915.	Wt. of large cups. G.	Δ. Mg.	Wt. of small cups. G.	Δ. Mg.	Treatment of cups.
June 10.....	80.293412	+0.004	38.495585	+0.003	Washed, dried and glowed
	404	-0.004	579	-0.003	Heated to dull redness
Mean, 80.293408		±0.004	38.495582	±0.003	
June 11.....	80.293183	+0.068	38.494855	+0.047	Washed and dried at 160°
	113	-0.002	805	-0.003	Heated to dull redness
	082	-0.033	788	-0.020	Heated to dull redness.
12.....	083	-0.032	786	-0.022	Heated to dull redness
Mean, 80.293115		±0.034	38.494808	±0.023	
Average Δ's of both sets,		±0.024		±0.017	

The results of Table II show very little change, if any, in the weight of the empty cup due to heating them to redness. In all the succeeding work the empty cups were glowed each time before weighing them.

When heating the cups with silver deposits to dull redness, the porcelain dish serving as a cover for the cup was examined for any traces of volatilized silver, but none was ever seen nor was any found by chemical tests. During the heating process the observer listened for the "series of small explosions" mentioned by Richards and Anderegg,¹ but this phenomenon was never observed.

(c) The Silver Voltameters were the same instruments as used in the previous work at the Bureau of Standards together with the voltameters previously used in the Princeton laboratory. To these were added two silver cups identical in size and shape with the Princeton platinum cups. It has generally been thought impossible in the past to use silver cups, partly because the deposit cannot readily be removed and the cup restored to its original condition, and partly because of inconstancy of weight when heated. Both of these objections were mentioned by Lord Rayleigh.² Recently it has been found in the work at Princeton that silver deposited on *highly polished silver* may be scraped off with the greatest ease, although it adheres sufficiently well for the usual washing operations. The deposit after being washed was scraped down while still wet with a small silver "hoe." This has afforded a ready means of determining the inclusions between the crystals and the cup and of saving deposits for further examination for inclusions. Prof. Hulett has kindly permitted us to make use of his silver cups in this way.

The electrolytes used in these experiments were generally of a very high

¹ *Loc. cit.*, p. 9.

² *Phil. Trans.*, 175, 411 (1884).

degree of purity and the silver nitrate was prepared either by the methods¹ previously described by the Bureau or by the Princeton method. The electrolyte was always tested for its acidity and for reducing agents.

The cups were weighed on the same balances described by Rosa, Vinal, and McDaniel,² but these balances were mounted in a new balance room, similar, however, to that used before.

3. The Alloying of Silver and Platinum.

Nearly all the previous observers who have tried heating the silver deposits have mentioned the alloying of the silver and platinum at a temperature corresponding to dull redness, and Van Dijk³ has described the black stain left on the platinum cup after the silver has been removed. Others have not mentioned this, probably because the stain was almost invisible if the alloying was slight. None of the previous authors seem to have been aware of the significance of this alloying and of the black stain; for example Richards and Anderegg⁴ say, "Such heating slightly alloys the two metals * * * * *". This complication, of course, had not the slightest effect upon the quantitative experiment."

Time, as well as temperature, is a very important factor in alloying. Rapid heating to a given temperature for a short time may produce little effect, but it becomes very pronounced as the time of heating is increased, as we found on using the electric furnace. A cup heated to 625° for thirty minutes in the furnace was much more alloyed than a similar cup heated to 675° in the same furnace and immediately allowed to cool.

When the deposits are removed from the alloyed cups by electrolysis or nitric acid, a brown stain remains on the platinum if the cups have been heated for only a short time with the flame, or a heavy, dark brown or black stain in the case of cups heated for a longer time in the furnace. We were unable to remove this stain completely by scrubbing without a considerable abrasion of the platinum surface and it persisted even after the cups were carefully washed and dried at 160°. If the cups were heated to bright redness in a Bunsen flame the slight stains completely disappeared, but their capacity to make trouble was only slightly lessened. Early in our work we found that this change in color from brown or black to gray was accompanied by a marked change in weight of the cup. This change in weight may be as small as 0.1–0.2 mg. in the case of cups that have been very slightly alloyed or it may amount to milligrams in case of heavily alloyed cups. The following figures give the change in weight as we have observed it for a few cases:

¹ *Bur. Standards Bull.*, 9, 537, reprint No. 201; *Trans. Am. Electrochem. Soc.*, 22, 372 (1912).

² *Bur. Standards Bull.*, 9, 174, reprint No. 195.

³ *Arch. Néerland. des. sci.*, [II] 10, 277 (1905); *Ann. Physik*, 19, 265 (1906).

⁴ *Loc. cit.*, p. 15.

TABLE III.

Change in weight due to glowing a cup stained by the alloying of silver and platinum after cleaning and drying at 160°.

Date. 1915.	Loss in wt. Mg.	Character of stain.
July 27.....	0.180	Very slight brown stains
	0.220	Very slight brown stains
Aug. 6.....	0.672	Brown stains
	0.643	Brown stains
Sept. 23.....	1.083	Brown stains rather prominent
Oct. 2.....	4.89	Heavy black stain

The cause of this phenomenon seems to be the expulsion of adsorbed material in the brown or black stains. These stains we believe to be platinum black. The nature of this material adsorbed by the platinum black has not yet been determined, but experiments will shortly be made to identify it. The disappearance of the stains when heated was more apparent than real, since the platinum black was converted into platinum gray and was, therefore, hardly visible on the gray surface of the platinum cup itself. The stains show their marked catalytic power when brought in contact with hydrogen peroxide. Even in cases when the alloying has been so slight that the platinum black stains are invisible we have found that the actual presence of the stains can be shown by making a test with peroxide. In this test the peroxide was made to cover both platinum black and the bare platinum surface of the cup at the top. The bubbles formed quickly in the platinum black region and not noticeably over the bare platinum. There was a sharp line of demarcation between the decomposing peroxide and the remainder at the point where the top of the silver deposit had been. We have also tried this experiment on a cup which had been heavily alloyed by heating in the furnace and in this case we found that the prominent brown stains caused a great evolution of bubbles in the peroxide. In another case the platinum black stains which had been converted into platinum gray by glowing the cup were tested. Here the effect was much less marked than in a companion cup which had been similarly treated in every way except that it had not been glowed. We think this indicated that the stains were really platinum black.

In the case of moderately alloyed cups, with polished inner surfaces, the brown stains often showed the position and size and shape of each individual crystal of silver. But as the alloying was increased by longer heating it was possible to see the alloy spread out into the spaces between the crystals of silver, so that when the silver was removed the brown stains had merged together forming one continuous stain all over the inner surface of the cup. We have examined these stains under a high power microscope and found them to be essentially a surface phenomenon.

It seemed desirable to investigate the change in weight of this platinum

black in its relation to temperature and, therefore, we heated a cup to successively higher temperatures, weighing it after each heating. As a trial we washed and weighed it three times, heating it to 151° to see how well the weighings might be expected to repeat themselves. The cup contained only a medium amount of the stain and was not an extreme case.

TABLE IV.

Wt. of cup minus counterpoise. Mg.	Temperature. $^{\circ}$ C.	Decrease in wt. Mg.	Remarks.
+0.276	151.	...	Heated in electric oven
+0.236	151	...	Heated in electric oven
+0.247	151	...	Heated in electric oven
+0.123	231	0.130	Heated in electric oven
+0.044	400	0.079	Heated in electric furnace
-0.660	600	0.704	Color changed to gray
-0.718	660	0.058	Heated in electric furnace
-0.830	760	0.112	Heated in flame, temp. estimated

Total, 1.083

These results are shown graphically in Fig. 1.

We next considered the question of the effect this layer of platinum black or platinum gray has upon the silver deposited and what role it played in the determination of the inclusions by the method of heating as advocated by Lord Rayleigh and later by Richards. From the above results we concluded that a cup containing a trace of platinum black, on which silver has been deposited, if heated to dull redness will show a loss in weight that cannot properly be assigned to the liberation of inclusions in the silver alone. Yet all previous observers, with little or no precautions to insure against the presence of the platinum black, have assumed the observed loss in weight to represent the liberated inclusion from the silver deposit. It is also obvious that if the platinum black is present the losses observed when making determinations of the inclusions by heating will be found to be very variable and their magnitude will depend upon the amount of platinum black present and its previous heat treatment. On the other hand if the cup had been glowd before making the deposit of silver, so that the platinum black is converted to platinum gray, it is less probable that subsequent heating of the silver deposit will show large or variable losses in weight. We have made a special test of this point in the case of two cups both coated with platinum black from previous alloying with silver. One of these was glowd before making the deposit of silver and the other was treated in the usual way, that is, washed and dried at 160° . Aside from the question of relative weights of the two deposits, which will be discussed farther on, we give here the observed losses in weight when the two cups with identical deposits were heated:

Cup that had been glowd before making the deposit, lost 0.06 mg.

Cup that had not been glowd, lost 4.89 mg.

This, of course, is an exaggerated case, but shows the possibility of error in the assumption made by previous observers as mentioned on page 502.

We concluded that if the cup has been thoroughly glowd previously to making the deposit that a subsequent determination of the inclusions will represent fairly the change in weight of the deposit. For if we take the mean of thirteen determinations given in Table VI, in which the

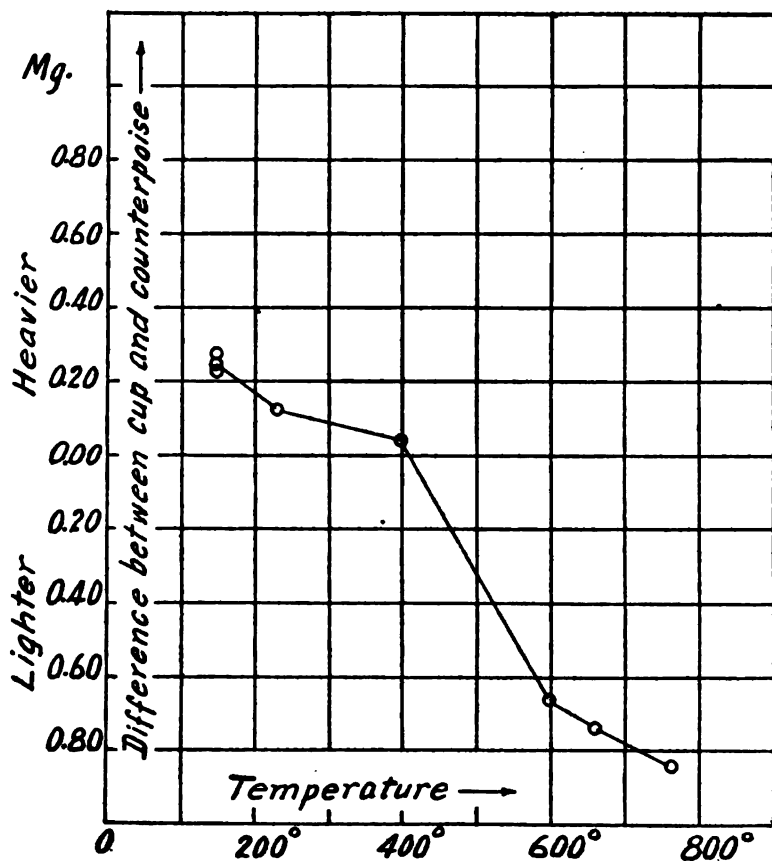


Fig. 1

cup contained a small amount of platinum black previously glowd, and compare it with twelve determinations made with cups which were entirely free from the platinum black or platinum gray before making the deposit, we find the difference in estimated inclusions to be only 0.0006% which is within the experimental error.

4. Effect of Alloying on the Amount of Silver Deposited.

The first intimation which we had that the presence of platinum black or platinum gray in the voltameter would cause serious errors in the quantity of silver deposited was in an early experiment when two cups that had been heavily alloyed, but subsequently glowd, showed deposits more than two milligrams lighter than the other cups. It was this experiment that first suggested the nature of the stains on the platinum and led us to experiment with them. Since then we have made special experiments to determine the general effect of previous alloying of the cups on subsequent deposits of silver.

TABLE V.

Effect of platinum black and platinum gray on the mass of silver deposited (deposits dried at 160°).

Date. 1915.	Cup.	Deposit. Mg.	Condition of the cup.	
Aug. 12.....	38	4249.23	Normal voltameter, no alloy	
	27	4249.19	Pt black removed by aqua regia	
	28	4250.61	A heavy layer of platinum black	
	18.....	93	4207.80	Normal voltameter, no alloy
		92	4207.33	Slightly alloyed and glowd
		27	4207.68	Pt black removed by aqua regia
		39	4207.49	Slightly alloyed and glowd
		1	4207.58	Pt black removed by aqua regia
		11	4207.64	Pt black removed by aqua regia
Oct. 2.....		27	4233.03	Alloyed and glowd, platinum gray
		28	4234.35	Heavy layer of platinum black
		38	4233.58	Normal voltameter, no alloy

It thus appears that a cup that had been alloyed and hence contains the platinum black stains gave an apparently heavier deposit than normal if it had not been glowd, or a lighter deposit than normal if it had been glowd previously to making the deposit. This was not understood at first since we thought that the light weight of the deposit might be due to the catalytic effect of the platinum gray on the hydrogen ions present in the solution, and it was, therefore, expected in the experiment of Aug. 12th that cup No. 28 would show a still lighter deposit. As a matter of fact the deposit was much too heavy and this was confirmed by the same cup in the experiment of Oct. 2nd. The difficulty was explained when we heated cups No. 27 and No. 28 of the last experiment to a dull red. No. 27 lost 0.060 mg.; No. 28 lost 4.89. That is, the deposit in No. 28 was in reality much the lightest, although apparently heavy, owing to material probably adsorbed by the platinum black.

Careful measurements of the acidity of the electrolyte were made and checked for the experiment of Oct. 2nd. It was found that the acidity increased considerably in the case of the cup with platinum black, somewhat less for the cup with platinum gray and none at all for the standard cup.

The acidities were as follows:

Initial acidity of electrolyte.....	7×10^{-4} acid
Final acidity No. 27, platinum gray.....	10×10^{-4} acid
Final acidity No. 28, platinum black.....	15×10^{-4} acid
Final acidity No. 38, normal cup.....	6×10^{-4} acid

Table V shows that when the platinum cup containing the platinum black is cleaned with cold concentrated aqua regia, and rubbed, the deposits are in agreement with those in cups which have never been alloyed with silver. This cleaning process, however, removes a considerable amount of the platinum. In exaggerated cases this is as much as a gram. For this reason it appears doubtful whether a moderate amount of scrubbing would suffice for the complete elimination of the platinum black. Richards and Anderegg, for example, mention scrubbing the cups and say that the crucibles lost a few tenths of a milligram each time. Our work would lead us to expect a much greater loss than this if the platinum black, even for only a slight alloying, be entirely removed. Cleaning the cups in this way is inconvenient and destructive to the cup. We do not find it necessary to make inclusion determinations for every deposit of silver and to do so would speedily ruin the platinum cups.

5. Estimation of Inclusions in Deposits from Pure Electrolytes.

Table VI shows the observed losses in weight of deposits from pure electrolytes, the purity being judged by the standards of purity previously published by the Bureau.¹ All such deposits which were heated according to the method described by Richards and Anderegg are included in this table. In no case was platinum black present, but in some cases slight amounts of platinum black had been converted over into platinum gray before making the deposits. This is immaterial, as we showed on page 503, but these cases are noted in the table. All deposits which were heated in the electric furnace are also included in the table, with the exception of two in the experiment of July 20th. For unknown reasons these were discordant with all the other results of the table and they are therefore omitted. They would affect the mean result by only 0.0005% if they were included.

The inclusions expelled by heating the silver, therefore, seem to be about 0.004%. Richards and Anderegg² apply a correction of 6% for the solids they estimate to remain from the inclusions, but 6% of 0.004% is too small to consider.

It is interesting at this point to compare the results which have previously been obtained by methods similar to those used in this paper. We give in Table VII an analysis of earlier results compared with our own. In general these results had to be computed from the original data con-

¹ *Bur. Standards Bull.*, 9, 524, reprint No. 201.

² *Loc. cit.*, p. 18.

TABLE VI.—ESTIMATION OF INCLUSIONS BY HEATING THE DEPOSITS.

Date. 1915.	Cup.	Method of heating.	Temper- ature, °C.	Number of heatings.	Total loss in wt. Mg.	Loss in wt. %.	Platinum gray pres- ent or not.	Remarks.
June 14	95	Flame	..	2	0.130	0.0032	No	Silver nitrate prepared by B. S. methods
	39	Flame	..	2	0.186	0.0045	No	Silver nitrate prepared by B. S. methods
	16	Flame	..	3	0.220	0.0055	Yes	Silver nitrate prepared by B. S. methods
	39	Flame	..	3	0.300	0.0075	Yes	Silver nitrate prepared by B. S. methods
24	95	Flame	..	3	0.181	0.0041	Yes	Silver nitrate as purchased not quite pure
	92	Flame	..	3	0.129	0.0029	No	Silver nitrate prepared by B. S. methods
	27	Flame	..	3	0.205	0.0047	No	Silver nitrate prepared by B. S. methods
	28	Flame	..	3	0.279	0.0064	No	Silver nitrate as purchased not quite pure
July 9	95	Flame	..	2	(+)0.007	(+)0.0002	Yes	Silver nitrate prepared by the Princeton method
	92	Flame	..	2	0.013	0.0003	Yes	Silver nitrate prepared by the Princeton method
	27	Furnace	625	2	0.048	0.0011	Yes	Silver nitrate prepared by the Princeton method
	28	Furnace	625	2	0.028	0.0007	Yes	Silver nitrate prepared by the Princeton method
I	I	Furnace	625	2	0.166	0.0040	No	Silver nitrate prepared by the Princeton method (Cup not previously glowd)
	II	Furnace	625	2	0.115	0.0028	No	Silver nitrate prepared by the Princeton method (Cup not previously glowd)
20	95	Flame	..	1	0.161	0.0037	Yes	Silver nitrate prepared by the Princeton method
	92	Flame	..	1	0.116	0.0027	Yes	Silver nitrate prepared by the Princeton method
	I	Furnace	623	1	0.322	0.0073	Yes	Silver nitrate prepared by the Princeton method
	II	Furnace	623	1	0.254	0.0058	Yes	Silver nitrate prepared by the Princeton method
Aug. 9	92	Flame	..	1	0.333	0.0079	Yes	Silver nitrate prepared by the Princeton method
	18	Furnace	625	1	0.240	0.0057	No	Silver nitrate prepared by the Princeton method
	I	Furnace	630	1	0.111	0.0026	No	Silver nitrate prepared by the Princeton method
	II	Furnace	625	1	0.169	0.0039	No	Silver nitrate prepared by the Princeton method
Oct. 2	27	Flame	..	1	0.060	0.0014	Yes	Silver nitrate prepared by B. S. methods
	13	Flame	..	1	0.251	0.0057	No	Silver nitrate prepared by B. S. methods
	28	Flame	..	1	0.238	0.0054	No	Silver nitrate prepared by B. S. methods
							Mean,	0.0040% ± 0.0018%

Probable error, 0.0015% for single observation; probable error, 0.0003% for mean result.

Mean flame determinations, 0.0041%; mean furnace determinations, 0.0038%.

tained in the various papers. Thus in the case of Lord Rayleigh's Table II we have computed the percentage loss in weight of the deposit for all deposits made from silver nitrate not contaminated with acetate. For Richards and Anderegg's work we have included all the results given in their Table III and have averaged them together.

TABLE VII.

Summary of Results Obtained by Heating the Silver Deposits in the Platinum Cups to Expel Inclusions.

Year.	Observers.	Extreme values.		Range. %.	Mean result. %.	No. of observations.
		%				
1884	Rayleigh & Sedgwick ¹	0.000	—0.030	0.030	0.010	24
1902	Richards and Heimrod ²	—0.003	—0.030	0.027	0.018	12
1906	Van Dijk ³	+0.009	—0.006	0.015	0.000	7
1908	Jaeger and von Steinwehr ⁴ ..	+0.002	—0.005	0.007	0.0008	18
1912	Boltzmann ⁵	+0.0026	—0.0087	0.0113	0.0028	19
1915	Richards and Anderegg ⁶ ...	—0.0039	—0.0352	0.0313	0.0148	27
1915	Vinal and Bovard ⁷	+0.0002	—0.0079	0.0081	0.0040	25

It is readily seen from Table VII that the results classify themselves in two groups. On the one hand we have Lord Rayleigh and Mrs. Sedgwick, Richards and Heimrod, and Richards and Anderegg; on the other hand we have Van Dijk, Jaeger and von Steinwehr, Boltzmann and the present authors. So far as Lord Rayleigh and Mrs. Sedgwick are concerned, it must be remembered that they were working with the filter paper voltameter and, therefore, their electrolyte was impure, which we think will account for a high value for the inclusions. Whether we include their results or not, the fact remains that Richards and his co-workers stand alone in finding the largest inclusions and in having the largest variation between his extreme values. The most consistent results, that is, those having the smallest difference between the extreme values are the results of Jaeger and von Steinwehr. These are closely followed by the results of the present paper and by the results of Boltzmann and Van Dijk. If we group these four series together we have 69 fairly consistent determinations, of the inclusions of which the mean is 0.0023%, weighting each of the four results according to the number of observations on which it is based. Richards' 39 observations, on the contrary, give a mean result of 0.0154% or nearly seven times larger than the mean of the other observers. Just how much effect the platinum black has had in the results of these previous observers we shall not attempt to say,

¹ *Phil. Trans.*, (A) 175, 438 (1884).

² *Z. physik. Chem.*, 41, 323 (1902).

³ *Ann. Physik*, 19, 266 (1906).

⁴ *Z. Instrumentenk.*, 35, 226 (1915).

⁵ *Sitzb. Akad. Wiss., Wien*, 121, 1062 (1912).

⁶ *THIS JOURNAL*, 37, 16 (1915).

⁷ *This paper*.

but it is evident that in the case of Van Dijk, Jaeger or von Steinwehr and Boltzmann it was very small. The last named mentions glowing the cup each time before making a deposit and this would nullify the effect of the platinum black so far as determining the inclusions is concerned, as we have shown.

The voltmeters used in the researches that showed very small inclusions have varied greatly in size. The smallest cup was Van Dijk's which held only 30 cc. and the largest were our own, some of which held over 300 cc.

Smith, Mather, and Lowry heated a few deposits, but not to as high a temperature as in the case of the results recorded in Table VII; they are, therefore, not mentioned in this connection. This is also the case with a few other observers whose methods have differed in principle from the methods of this paper.

6. The Value of the Faraday.

The Bureau¹ published some years ago a value for the absolute electrochemical equivalent of silver which was obtained by the same silver voltmeters used in the present work and an absolute current balance. This value was 1.11804 mg. per coulomb. Subsequently this was revised² to 1.11805 mg. per coulomb. Whichever of these values is taken, if we apply as a correction the estimated inclusions as found in the preceding section, it appears that 1.11800 mg. per coulomb, which was adopted by the London Electrical Congress of 1908 as the value for the electrochemical equivalent in determining the International ampere, is in reality also the closest figure that we can assign as an absolute value to this constant and is probably correct to within a few parts in one hundred thousand. We do not know the value for the atomic weight of silver with this degree of accuracy. It is only expressed to five significant figures, but taking the present international value 107.88 we find the value of the Faraday to be

96,494.

In a recent paper by Vinal and Bates³ the value 96,500 is recommended for general use and this recommendation still holds good. The correction for inclusions found in the present paper will account for only four out of twenty-one parts in 100,000 difference between the results of the silver and iodine voltmeters of their work. Additional experiments are now being made in the Princeton laboratory in which some of the deposits obtained during the present investigation will be analyzed. After these results have been obtained a more extensive discussion of the Faraday will be given.

¹ *Bur. Standards Bull.*, 8, 367, reprint No. 171.

² *Ibid.*, 10, 477, reprint No. 220.

³ *Ibid.*, 10, 449, reprint No. 218.

7. Additional Experiments on the Deposits.

(a) **Successive Heatings of the Deposits.**—It will be noted in Table VI that some of the deposits were heated more than once. This was to determine how completely the inclusions are expelled by one heating. Our experiments showed that about 90% of the total loss in weight occurs the first time that they are heated.¹ The second and third heatings show small changes, which are sometimes slight gains in weight instead of losses.

(b) **Effect of Heating Deposits to an Abnormally High Temperature.**—Two deposits were heated by a flame to a temperature estimated at 700° after being heated to dull redness. The resulting loss in weight was observed.

Percentage of deposit, 0.0017 and 0.0006. Mean, 0.0011%.

One deposit was heated in the furnace to 675° after having been twice heated to 625°; the result was an apparent gain in weight of 0.0011%.

Effect of Prolonged Heating of the Deposit.—When the deposits are heated with the Bunsen burner the time that the deposit is at a high temperature is very brief, but in the case of the furnace the cup and deposit are over 600° for at least 7 minutes. The agreement of these two methods of heating shows that the time is not significant, but as a further test we baked a deposit for the second time in the furnace for 1/2 hour at 625° and found the loss in weight to be only 0.0004%.

It is fortunate that the time for heating can be made so short because the trouble with the alloy of silver and platinum is much lessened.

(c) **Heating the Deposit after Removal from Cathode.**—Two samples A and B of silver deposits from pure electrolytes were removed from the silver cathodes as described on page 499. These were dried at 160° in a small platinum dish previously washed, dried, and glowed. After weighing they were heated in the same platinum dish to dull redness with a Bunsen burner. We give in Table VIII these two values, together with the values obtained by heating the deposits on platinum of the same run according to the method described by Richards, or in the furnace. Two deposits of the run of July 9th, which are given in Table VI, are omitted here because the platinum cups were not previously glowed, and two deposits also on June 24th made with a different electrolyte.

TABLE VIII.

Estimations of inclusions in silver scraped from the cathode.

Date. 1915.	Sample.	Loss in wt. %.	Cup.	Loss in wt. %.	Mean. %.	Difference, sample minus cup. %.
June 24.....	A	0.0045	92	0.0029	0.0038	+0.0007
			27	0.0047		
July 9.....	B	0.0008	95	(+)0.0002		
			92	0.0003		
			27	0.0011	0.0005	+0.0003
			28	0.0007		

¹ Boltzmann (*Loc. cit.*) also obtained a similar result.

The agreement of these two results is better than was to be expected.

(d) **The Inclusions between the Crystals and the Surface of the Cup.**—Richards and Anderegg¹ note that platinum cups with rough interior surfaces considerably increase the inclusions. It, therefore, seemed worth while to examine this point closely because of the excellent agreement of results obtained by Hulett and Vinal,² although one used platinum cups with rough interior surfaces and the other smooth surfaces. In the present work Cups I and II had rough interior surfaces and 27 and 28 became roughened after cleaning with the aqua regia, so we may readily classify the results given in Table VI according to the character of the interior surface of the cup. This is done in Table IX.

TABLE IX.

Comparison of inclusions in voltameters with rough and smooth surfaces.

Smooth surfaces (% loss in weight on heating):

0.0032, 0.0045, 0.0055, 0.0075, 0.0041, 0.0029, 0.0047, 0.0064, +0.0002, 0.0003, 0.0011, 0.0007, 0.0037, 0.0027, 0.0079. Mean, 0.0037%.

Rough surfaces (% loss in weight on heating):

0.0040, 0.0028, 0.0073, 0.0058, 0.0057, 0.0026, 0.0039, 0.0014, 0.0057, 0.0054. Mean, 0.0044%.

The difference is thus only 0.0007%, which is within the experimental error, and, therefore, we may say that the inclusions on smooth and rough surfaces are, so far as our experiments go, the same.³

As to the magnitude of the inclusions between the crystals and cup, we were enabled to form an estimate using the silver cups in which the silver can be so easily scraped from the cathode while the cup is filled with conductivity water.

The general procedure was to wash these deposits until further washing produced no change in the conductivity of the water used. Then a platinum cup similar to the cups in use was filled, after washing, with the same conductivity water and stood beside the cup under test. A large glass plate was interposed between the observer and the cups while the silver was scraped down, so that during the three to five minutes required the breath of the observer might not contaminate the water in the cups. As soon as the scraping was complete the conductivity of the water in the cup under test and the blank also were immediately measured in a conductivity cell of the pipet form.⁴ The net result found represents the increase due to the silver nitrate liberated by scraping the silver and also all other causes of increase of conductivity, except the effect of temperature which was under control. Consequently the values found are maximum values

¹ *Loc. cit.*, p. 16.

² *Bur. Standards Bull.*, 11, 557, reprint No. 240.

³ Compare Jaeger and von Steinwehr, *Z. Instrumentenk.*, 35, 233 (1915).

⁴ This was the same cell used by Hulett and Vinal, *Bur. Standards Bull.*, 11, 558, reprint No. 240.

and the silver nitrate calculated from the increase in conductivity is probably too large. In the first experiment the value found is considerably larger than in the others. This is probably due to imperfect technique before we learned the best way of doing the experiment. The results are given in Table X.

TABLE X.
Inclusions between crystals and cup.

Date, 1915.	Cup.	Equivalent AgNO ₃ for increase in conductivity. Mg.
Aug. 9.....	VI	0.04 (omitted from mean)
	V	0.01
" 18.....	V	0.0052
	VI	0.0078

Mean, 0.0076 mg., 0.0002% of the deposit

The amount of silver nitrate trapped behind the crystals is, therefore, very small and consequently it is not surprising that Table VIII shows so close an agreement between the inclusions determined for the silver removed from the cathode and otherwise.

(e) **Inclusions in Silver Deposits from Less Pure Electrolytes.**—In two experiments we used electrolytes manifestly less pure than in the other experiments. For one of these we purposely added filter paper to the electrolyte and in the other the impurity manifested itself by a considerable volume effect which, being larger than the average experimental error, we regard as evidence of impurity. These results are given in Table XI.

TABLE XI.

Estimated inclusions by heating the cups with deposits from impure electrolytes.

Date, 1915.	Cup.	Loss in wt. %.	Remarks.
July 2.....	95	0.0067	Filter paper put in electrolyte
	92	0.0118	Filter paper put in electrolyte
	27	0.0071	Filter paper put in electrolyte
	28	0.0097	Filter paper put in electrolyte
28.....	95	0.0106	Volume effect of 7 in 100,000
	92	0.0102	Volume effect of 7 in 100,000
	27	0.0118	Volume effect of 7 in 100,000
	28	0.0095	Volume effect of 7 in 100,000
	1	0.0102	Volume effect of 7 in 100,000
	2	0.0093	Volume effect of 7 in 100,000

Mean, 0.0097

The inclusions, therefore, appear to be more than twice what was found in the case of pure electrolyte. This is in accord with the view expressed by the Bureau¹ several years ago that the presence of impurities of a colloidal nature which break up the crystalline structure of the silver will increase the inclusions in the deposited silver.

¹ *Bur. Standards Bull.*, 10, 517, reprint No. 220.

TABLE XII.
Analysis of deposits with reference to the volume effect.

Date. 1915.	Size.	Deposit before heating. Mg.	Δ. Large— small. Mg.	Deposit after heating. Mg.	Δ. Large— small. Mg.	Remarks.		
June 14	Large	4095.69	+0.12	4095.56	+0.17	Silver nitrate as purchased Filter paper in electrolyte Note volume effect		
	Small	4095.57		4095.39				
	16	Large	3975.84	+0.21	3975.62		+0.29	
		Small	3975.63		3975.33			
	24	Large	4375.07	+0.07	4374.94		+0.14	
		Small	4375.00		4374.80			
July 2	Large	4375.25	+0.15	4375.07	+0.25		Silver nitrate as purchased	
	Small	4375.10		4374.82				
	9	Large	4221.87	+0.97	4221.59		+0.99	Filter paper in electrolyte
		Small	4220.90		4220.60			
	9	Large	4222.46	+1.53	4221.98		+1.46	Note volume effect
		Small	4220.93		4220.52			
	9	Large	4180.13	±0.00	4180.14		+0.06	
		Small	4180.13		4180.08			
	9	Large	4180.09	—0.04	4180.08		—0.02	
		Small	4180.13		4180.10			
	28	Large	4339.94	+0.28	4339.48		+0.33	
		Small	4339.66		4339.15			
	Large	4339.84	+0.34	4339.40	+0.31			
	Small	4339.50		4339.09				
Total Δ's,			+3.63		+3.98			

(f) **The Volume Effect.**—Richards and Anderegg,¹ explaining the volume effect, attribute it to a surface effect and claim the inclusion to be greater in the larger cups, so that when both large and small cups are heated the resultant deposits are in agreement. We have examined all our experiments with this point in view and we give in Table XII an analysis of all those in which a comparison of our large and small cups (No. 92 and No. 95 large size, No. 27 and No. 28 small size) was made with subsequent heating, except for the experiment of July 20th, in which, as we stated on page 505, the results with the small cups were anomalous. This table includes the results of deposits from pure solutions in which the volume effect was very small or absent altogether and also the results of deposits from impure solutions in which the volume effect is large. The table shows that heating the deposits to expel the inclusions did not make the difference between large and small deposits any less² as Richards' theory would call for, but on the other hand the difference became a trifle larger, on the average 0.03 mg. for each comparison which is perhaps as good

¹ *Loc. cit.*, p. 16.

² Examining the results of Lord Rayleigh and Mrs. Sedgwick we find the same thing. Their large cup deposits lost 0.013% and their small cup deposits lost 0.009%. The difference between these results is well within their experimental error.

an agreement as could be expected. Richards' results could, however, be explained on his theory by the assumption that the platinum black from previous heatings was not entirely eliminated before making the deposit. In such a case for two cups equally alloyed the amount of platinum black would be proportional to the surface of the cup. This, even with pure electrolyte, would probably show an apparently heavy deposit in the large cup as our results on page 504 indicate and this deposit would also lose the most on heating to a high temperature, hence the two deposits would appear to draw together. The results of Table XII emphasize the previous viewpoint of the Bureau that the purity of the salt used for the electrolyte is the determining factor in the volume effect.

8. Experiments on the Anode Liquid.

Many lines of evidence led the Bureau to the conclusion stated in Part I¹ of the recent voltameter papers that the effects of the supposed anomalous substance formed at the anode during electrolysis were in reality due to impurities present in the solution, as for example filter paper. The Bureau has not found it necessary to change this view, but in the present work we have tried two further experiments on the anode liquid.

The first experiment was suggested to us by the remark of Richards and Anderegg² that the reasons most observers had failed to find this peculiar compound in the anode liquid, is because they delayed testing for it until the compound had become oxidized and vanished. Accordingly, we drew four 10 cc. samples of the dense anode liquid (17%, the original electrolyte was 10%) from inside the porous cups of the voltameters of Aug. 18th. The electrolyte of this experiment was quite pure as judged by the permanganate, acidity and volume effect tests. The four samples of anode liquid were taken within one minute after the electrical circuit was broken. Each was put in a stoppered glass tube and acidified, then one cc. of 0.001 *N* KMnO_4 was added to each tube and all shaken to mix the contents. The whole operation consumed less than five minutes. The times required for the permanganate color to fade were noted. They were

42; 52; 70; 70; mean, 59 minutes.

We do not think that our anode liquid contained the oxidizable compound spoken of by Richards, else the color of so small a quantity as 1 cc. of 0.001 *N* KMnO_4 would hardly be expected to last for an hour.

Our second experiment on the anode liquid was suggested by the use of the alundum porous cups in an experiment described by Richards and Anderegg.³ They used the porcelain porous cup to hold back the anode compound and the very porous alundum cup to let it through. We thought

¹ *Bur. Standards Bull.*, 9, 151, reprint No. 194.

² *THIS JOURNAL*, 37, 686 (1915).

³ *Ibid.*, 37, 685 (1915).

that a slightly different arrangement of the porcelain and alundum cups would perhaps throw more direct light on the matter. A previous experiment showed that our alundum cup permitted water to pass through its pores about sixty times as fast as it passed through our porcelain (Pukal) porous cups.

We arranged three voltmeters. One was a normal voltmeter with the ordinary porous cup, the second was similar to the first except that an alundum porous cup was used in place of the porcelain porous cup. The third had a porcelain porous cup fitting snugly inside of an alundum porous cup. The alundum and porcelain cups were all prepared similarly and as described by the Bureau.¹ According to the theory of Richards, the deposits in the first and third voltmeters should agree and both be lighter than the deposit in the second, but on the other hand if the heavy anode compound with excess silver is non-existent then the second and third should agree and if heavier than the first this shows that the alundum cups are responsible for introducing impurities into the solution. The results of this experiment were as follows:

	Mg.
The first (normal voltmeter).....	4327.08
The second (alundum cup).....	4327.38
The third (alundum cup with porcelain porous cup inside).....	4327.44

These results, therefore, tend to confirm the previous views of the Bureau that the anode reactions produce no effect whatever in the quantitative measurements² of the silver deposited.

This work has been done at the Bureau of Standards under the direction of Dr. E. B. Rosa. We have also been fortunate in having the help of Prof. G. A. Hulett. The investigation is being continued under the direction of Prof. Hulett by one of the present authors (Bovard) in the Princeton laboratory.

9. Summary.

(1) We have heated a number of silver deposits to temperatures slightly above 600° both with a flame and in an electric furnace and have found the losses in weight to indicate inclusions of foreign matter in the deposits to be 0.0040% on the average for pure electrolyte and higher for impure electrolytes.

(2) We have found that such heating of the deposits produces an alloy of silver and platinum, which, when the silver is dissolved, leaves a layer of platinum black that may lead to serious errors the next time the cup is used if proper precautions are not taken.

(3) We are led to conclude that the most accurate absolute value for the electrochemical equivalent of silver is 1.11800 mg. per coulomb and,

¹ *Bur. Standards Bull.*, 9, 185, reprint No. 194.

² Boltzmann (*Loc. cit.*) made experiments on the anode liquid and also found it without effect on the deposited silver.

therefore, the value of the Faraday becomes 96,494 absolute coulombs, but for general purposes 96,500 as a round number is recommended.

(4) Inclusions in silver deposits made on smooth platinum surfaces are the same to within the experimental error as when the deposits are made on matte surfaces.

(5) Inclusions between the crystals and cup have been measured by an application of the conductivity method and are found to be a negligible part of the total inclusions which, with pure solutions, were about four parts in a hundred thousand.

(6) In cases where the deposit in large cups exceeds that in small cups (that is where the "volume effect" is appreciable) we do not find that strong heating of the deposits diminishes the difference.

(7) Two experiments on the anode liquid support the Bureau's previous conclusions as to the non-existence of the heavy anode ion.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY.]

STUDIES OF THE VAPOR PRESSURE OF SOLUTIONS. THE LOWERING OF THE VAPOR PRESSURE OF WATER PRODUCED BY DISSOLVED POTASSIUM CHLORIDE.

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Introduction.

In a preliminary article¹ the authors described a static method for the study of the vapor tension of aqueous solutions, and gave a sufficient amount of experimental material to demonstrate its reliability. Although these results were apparently very good, when judged by the agreement among the different determinations made on a given solution at various times, extending over periods of several weeks, the authors were not positive that the results obtained were the true vapor tension depressions of the solutions investigated. For this reason certain alterations have been made in the apparatus as originally described. In its improved form it is believed that the apparatus is capable of giving the vapor tension depressions of aqueous solutions correctly to 0.001 mm. or less; and in the present article the authors purpose to describe these alterations in detail and with as little repetition of the portion contained in the first article as will make the description clear. The accompanying illustrations, in which all essential details of the apparatus are given, will assist in making clear such points as are not described here in detail. The measurements on potassium chloride solutions recorded in

¹ THIS JOURNAL, 36, 2439 (1914); also *Z. physik. Chem.*, 89, 155 (1914).

this article, have been made under these improved conditions and are considered by the authors to be reliable.

The principal changes made in the apparatus are (1) the alterations of the thermostat and thermoregulator designed to secure a more nearly constant temperature, and (2) the introduction of a method for the continuous stirring of the solvent and solutions while in a vacuum.

The Apparatus.

Thermostat.—Fig. 1 shows the construction of the constant temperature bath as seen in cross-section. The bath proper is a cylindrical copper vessel 56 cm. high and 61 cm. in diameter, which rests on a wooden shelf supported by four heavy upright timbers as shown. The arrangement of the interior is such that three separate systems are symmetrically located in the bath, one of which contains the pure solvent, water, and the remaining two, the solutions under investigation. The two bulbs for solutions are shown at F and G. A is a $1\frac{1}{4}$ H. P. vertical motor of 560 revolutions, the shaft of which is elongated and at B is coupled directly to the propeller shaft C. The propeller D rotates inside the copper cylinder E, which can be raised or lowered and fixed at any desired height on the upright supports, fastened to the bottom of the bath and passing through slots on the side of E. Directly beneath the propeller is situated the compartment L, which is open beneath for the introduction of the electric light N, the source of heat used. About midway between the lateral walls of E and L are fixed the 12 mm. copper coils for the circulation of cool water, the entrance to which is seen at J and the exit at I. At HH are seen two of the vertical plates which are fixed to the interior of E, the purpose of which is to prevent the rotation of the water within E, and thus to provide for more rapid motion of the water upward through the cylinder. In this way a very rapid stream of water is constantly drawn from the bottom of the bath, upward through E and distributed uniformly at the top of the bath, flowing outward and downward over the coils of the thermoregulator R (to be described later) and the bulbs containing the solvent and solutions. By this method of rapid stirring in a symmetrical bath, the temperature of which changes extremely slowly, all parts of the bath are subjected to the same temperature conditions. The form and position of the very sensitive regulator R provides for the control of the temperature within narrow limits over long periods of time, as will be shown by records later on.

The temperature of the bath is maintained by means of the stove N, controlled by R, and the slow stream of cold water flowing through J. The capacity of N is as small as permissible, and the flow of water through J is made such that N will always supply to the bath an amount of heat slightly greater than is withdrawn by the current of water. In order to maintain the same temperature conditions in the bath, when the tem-

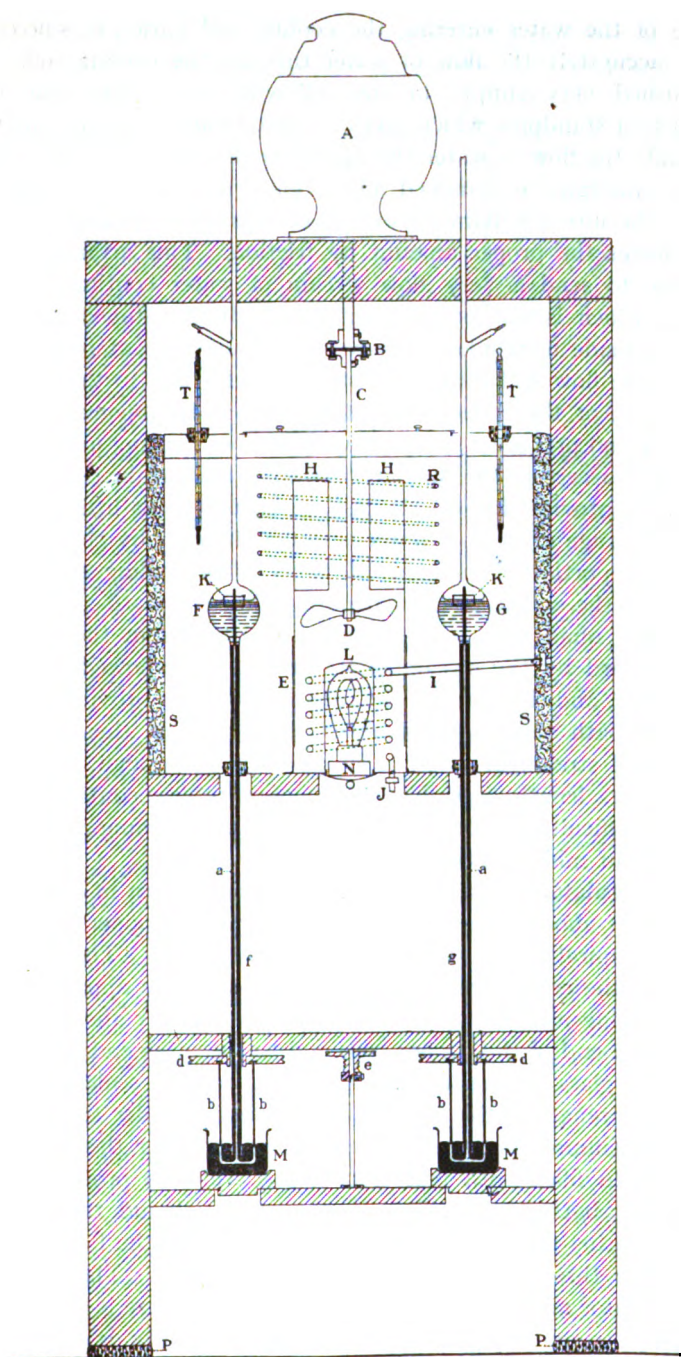


Fig. 1.

perature of the water entering the cooling coil varies, it is necessary to regulate accurately the flow of water through the cooling coil. This is accomplished very simply in the following way: Hydrant water is supplied to a standpipe which gives a constant head of water on the coil. To regulate the flow of water through the coil a section of the water pipe near the standpipe is removed and a glass tube about 25 cm. long inserted. The internal diameter of this tube is small enough to reduce the flow of water the proper amount by friction. This arrangement makes it possible to send a very slow stream of water continuously through the coils, which is not possible with an ordinary stopcock. When the attempt is made to regulate a very slow stream of water by means of a stopcock, the flow will ultimately stop entirely, due to the separation of dissolved air, or the collection of sediment, at the opening of the stopcock. One can prepare a series of such tubes of varying internal diameter and by trial ascertain the diameter required by certain temperature conditions and provide for all desired variations with little trouble. To avoid the change of flow of water through the coil, by the accumulation of air in any portion of the tube, all parts of the cooling system from the standpipe to the exit from the bath are inclined upward at a slight angle so that such quantities of air as may separate from the water will be carried forward by the stream of water and not allowed to accumulate in the system, and thus change the rate of flow. To provide for the maintenance of bath temperatures lower than that of the hydrant water the regulated stream of water is made to pass through a coil of about 4 or 5 meters length of thin-walled copper tubing contained in an ice bath. No difficulty has been encountered in maintaining a bath temperature of 20° in midsummer.

Thermoregulator.—The thermoregulator R is shown in detail in Fig. 2. It is made of about 5 meters of very thin-walled copper tubing bent in the form of spiral about 32 cm. diameter, as shown. The connection at A, between the copper coil and glass portion of the apparatus, is made in the following manner: A short, platinum cylinder about 3 cm. long is brazed to the end of the copper coil; and to the other end of the platinum cylinder the glass portion of the apparatus may be sealed without difficulty. To strengthen this connection a brass cylinder somewhat longer than the platinum cylinder is placed in position over the latter, and the space between filled with plaster of Paris, which is protected from the water of the bath by paraffin. The copper coil and the glass portion of the apparatus up to the level of the mercury in the bulb C, are filled with toluene through B, which is then sealed off. The filling of the thermoregulator must take place when the temperature is near that which it is desired to maintain in the bath. The regulator is then suspended by means of three supports (not shown on the drawing) to the top of the

copper cylinder E (Fig. 1), and when the bath temperature is sufficiently near that desired, pure mercury is introduced until its level stands at the desired point in D. Either platinum or tungsten wire may be used as the adjustable contact at N. The side-tube G is for the introduction of a continuous stream of pure hydrogen which aids greatly in maintaining the mercury surface at the point of contact clean.

The gradual fouling of the mercury surface makes it necessary at intervals of 2 or 3 weeks to withdraw a little of the mercury in D and replace it with fresh mercury—an operation requiring only a few minutes. No attention other than this is given to the thermoregulator for periods of a year or more. With this arrangement, as constructed by the

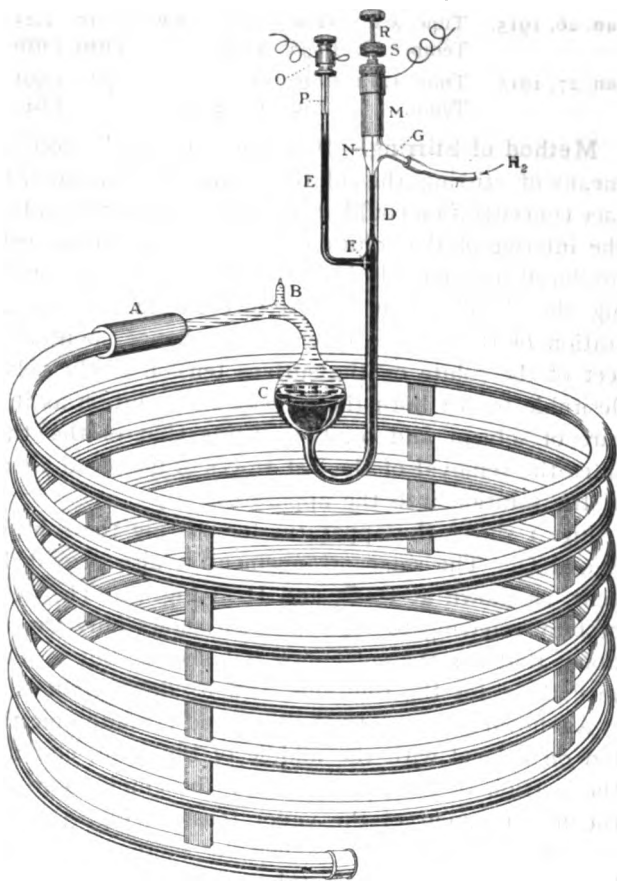


Fig. 2.

authors, a certain amount of the mercury in the vertical tube D was outside the thermostat and subject to the influence of the temperature of the room rather than that of the thermostat. As a result there was observed an occasional change in the temperature of the thermostat from day to day of not more than 0.002° or 0.003° . This occurred only when there was a marked change in the temperature of the room, and was always provided against when actual measurements were being made. In the case of all measurements here recorded a Beckmann thermometer immersed in the bath showed either no change or a change not exceeding 0.001° over the period of twelve hours during which observations were made.

The following record of the temperature of the thermostat will serve

to show the accuracy of regulation which was secured during the interval when measurements were being made. The temperatures are as read on a Beckmann thermometer:

Jan. 26, 1915.	Time, A.M.:	11.00	11.30.	P.M.:	12.10	2.25	3.05	3.25	4.00	5.10
	Temp. °:	1.650	1.650		1.650	1.650	1.650	1.650	1.650	1.650
Jan. 27, 1915.	Time, A.M.:	10.10	10.45	11.15.	P.M.:	12.01	2.00	2.55	3.45	4.35
	Temp. °:	1.649	1.649	1.649		1.649	1.649	1.649	1.649	1.649

Method of Stirring.—It seemed absolutely necessary to provide some means of stirring the solutions while in a vacuum, in order that the surface concentration could at all times be maintained the same as that within the interior of the solution. Changes in surface concentration might be produced by removal of some of the solvent during the process of eliminating the dissolved air as described in our previous article, or the concentration of the surface layer might change spontaneously, due to the effect of the solute on the surface tension of the solvent. It is also very desirable to stir both the solvent and solution as it insures the temperature of solvent and solutions being that of the thermostat, and facilitates the removal of the last traces of dissolved air after the introduction of the solution into the apparatus.

Fig. 1 shows the apparatus for stirring the solutions in the two bulbs F and G. The same arrangement is also provided for stirring the solvent, as shown at F, G, and H in Fig. 3. The device can be described best by referring to Fig. 1, which shows only the two systems for solutions; that for the solvent is not shown, but is identical in all respects with those for the solutions, and its description is unnecessary.

As shown in Fig. 1, the bulbs F and G containing the solutions are situated on a level with the middle of the bath, communicating above with the portion of the apparatus for the elimination of dissolved gases and the measurement of the vapor tension (Fig. 3), and below with a tube 16 mm. diameter and somewhat more than barometric height. The lower open ends of these tubes, *f* and *g*, dip beneath the surface of the mercury contained in the glass vessels M, M. The whole apparatus is completely exhausted and, after the preliminary removal of the greater part of the dissolved air in closed glass vessels, as described in our original article, the solution is left in the glass vessel (Fig. 4), under a partial vacuum. The transfer of the solution from the flask to the solution bulb F or G, as the case may be, is accomplished in the following manner to avoid contact with air: File marks are made on the glass tubes A and C (Fig. 4). One end, A, is connected by means of a rubber tube to a reservoir filled with clean mercury, care being taken to see that the rubber tube is completely filled with mercury, and that A is well immersed in the mercury at the open end of the rubber tube before A is broken off. When these precautions are taken the space in the flask (Fig. 4) not filled by solution,

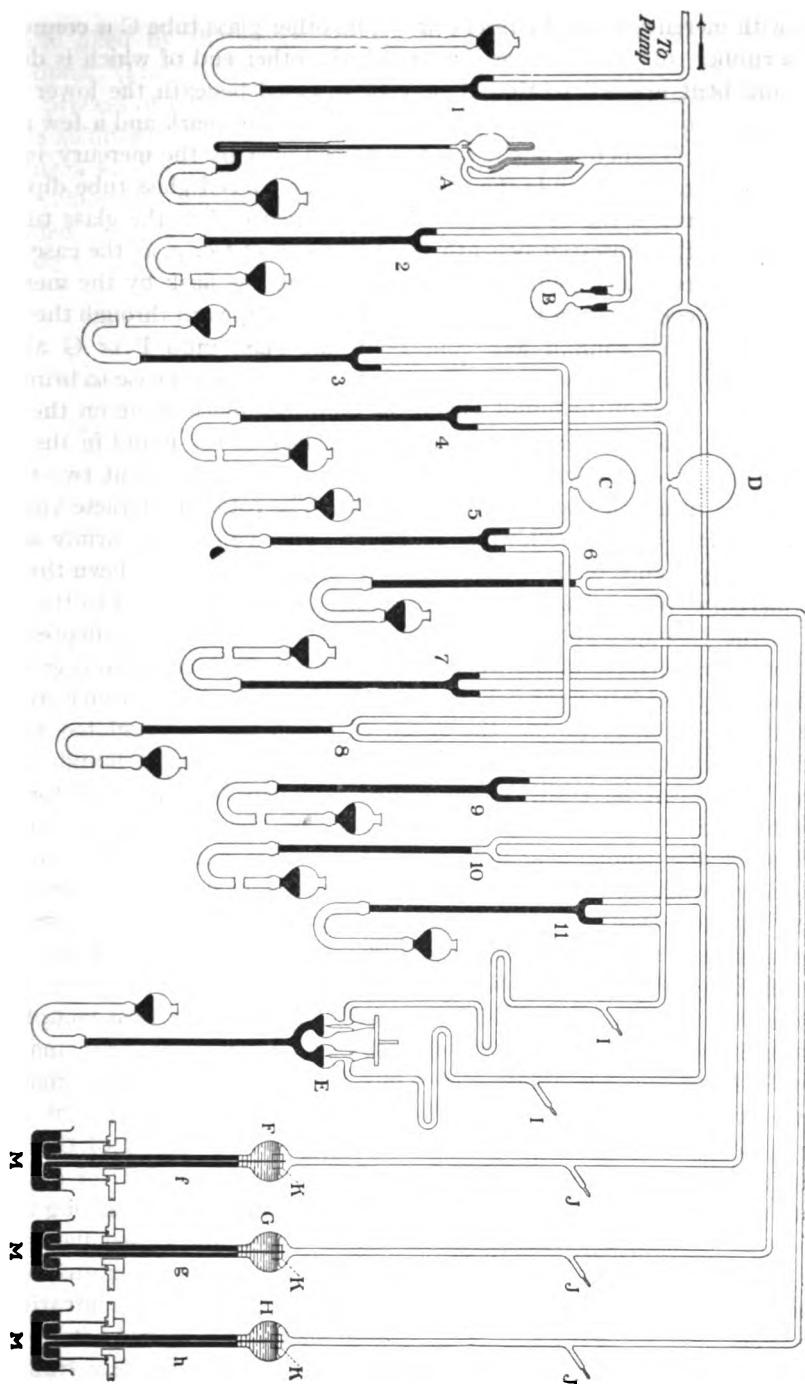


Fig. 3.

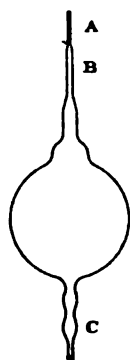


Fig. 4.

fills with mercury from the reservoir. The other glass tube C is connected by a rubber tube to a strong glass tube, the other end of which is drawn out and bent upward so that it may be inserted beneath the lower ends of *f* and *g*. C is broken off at the file mark and a few cubic centimeters of the solution forced over by the mercury in the reservoir while the open end of the curved glass tube dips beneath the mercury in M. The open end of the glass tube is then inserted beneath the lower end of *f* or *g*, as the case may be. The solution is then forced from the flask by the mercury contained in the reservoir, and passes upward through the mercury column and collects in the glass bulb F or G above. Care is taken to introduce just enough in each case to bring the level of the liquid within the bulb to a mark made on the outside of F and G. When the surface of the liquid in the bulb is at this level, the platinum vanes K, K are about two-thirds immersed in the liquid within. The rotation of these vanes is accomplished in the following manner: The vanes are firmly sealed into the upper ends of the long glass rods *a, a*, which extend down through the mercury columns in *f* and *g*, and at the bottom are sealed to the middle of the U-shaped rods *b, b*. The upper ends of *b, b* fit into depressions on the under surfaces of the wooden pulleys *d, d*, each of which is grooved and belted by a very light belt to the central loose pulley *e*, which in turn is belted to a small motor, the speed of which can be regulated within wide limits. In this way the simultaneous stirring of the liquids in all three bulbs can be easily accomplished and can be continued for any length of time without any thermal effect on the solutions or solvent, and while the whole system is evacuated. It is not necessary to provide any means of keeping these stirring devices in position as the buoyancy of the glass rods *a, a* in the mercury is sufficient. No trouble whatever has been experienced from the apparently fragile character of this device. It only requires careful construction in the beginning. The whole arrangement is so satisfactory that, when air has been completely removed, equilibrium is apparently established in the Rayleigh manometer E (Fig. 3), within the time (3-5 min.) required to adjust the manometer for a reading. Readings, however, are never taken until after the lapse of fifteen or twenty minutes after the adjustment of the traps and it has been shown that subsequent readings for periods of days do not vary from these first readings by more than the variations among themselves. During the preliminary removal of air in the closed flasks and the complete removal of air after introduction into the apparatus, a certain amount of water is removed from the solution, the concentration of which is thereby increased. The amount of water removed after introduction into the apparatus can be calculated quite accurately from the

volume filled by the vapor at each exhaustion and the number of exhaustions. The change of concentration of the solution during the complete process of removing the dissolved air has been determined on many of the solutions of potassium chloride investigated in this article by evaporating a known weight of the solution and weighing the residual potassium chloride. The greatest change of concentration observed corresponded to a change of 0.0002 mm. in the vapor tension of the solution, and we have made no correction for it on account of the small change.

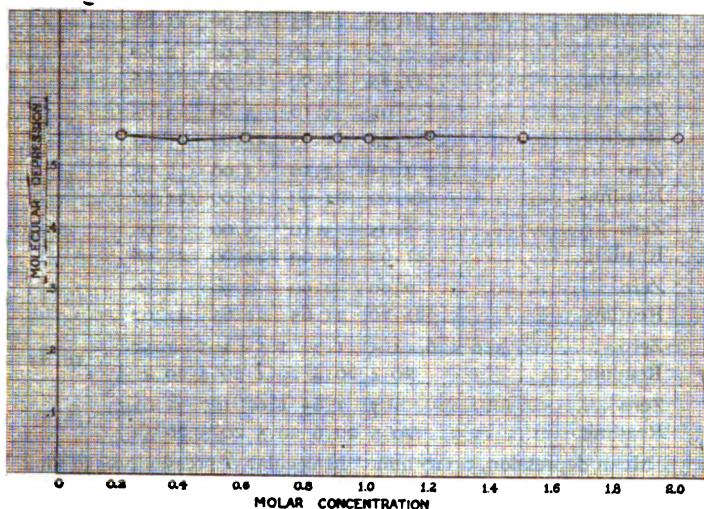


Fig. 5.

It will be noticed that the plan of the apparatus as shown in Fig. 3 is somewhat different from the former apparatus. This is due to the fact that the capacity of the apparatus has been doubled by introducing two systems for solutions and to the fact that each system has been made independent of the other two.

The results obtained from a study of aqueous solutions of potassium chloride at 20° are given below and are summarized in the ensuing table and curve. The concentrations employed here express the number of gram molecules of solute dissolved in 1000 grams of solvent.

Experimental.

1915		Experiment using 0.2 M KCl				Final observations as follows:		
						Mean.	Deflection.	Depression.
May 4	Zero.....	3.50	3.40	3.30	3.40	22.35	18.95	0.1105
	Reading.....	22.40	22.40	22.25	22.35			
	Zero.....	3.05	3.00	3.10	3.05	21.83	18.78	0.1095
	Reading.....	22.00	21.80	21.80	21.83			

					Mean.	Deflect.	Depres.
May 5	Zero.....	3.25	3.30	3.20	3.25	18.77	0.1095
	Reading.....	22.00	22.05	22.00	22.02		
	Zero.....	3.25	3.30	3.20	3.25	19.08	0.1113
	Reading.....	22.25	22.40	22.35	22.33		
	Zero.....	3.25	3.30	3.20	3.25	18.77	0.1095
	Reading.....	21.90	22.15	22.00	22.02		
May 6	Zero.....	2.90	2.90	2.90	2.90	19.08	0.1113
	Reading.....	22.15	22.00	21.80	21.98		
	Zero.....	2.85	2.90	2.90	2.88	19.00	0.1108
	Reading.....	21.90	21.85	21.90	21.88		
	Zero.....	2.85	2.90	2.90	2.88	19.00	0.1108
	Reading.....	21.85	21.90	21.90	21.88		
	Zero.....	3.05	3.10	3.00	3.05	18.88	0.1102
	Reading.....	21.95	21.95	21.90	21.93		
	Zero.....	3.05	3.10	3.00	3.05	18.93	0.1104
	Reading.....	22.00	21.90	22.00	21.98		
	Zero.....	3.05	3.10	3.00	3.05	18.93	0.1104
	Reading.....	21.90	22.00	22.00	21.98		
June 9	Zero.....	2.90	2.90	2.90	2.90	18.77	0.1095
	Reading.....	21.70	21.65	21.65	21.67		
June 9	Zero.....	1.6	1.6	1.5	1.5	18.83	0.1098
	Reading.....	20.4	20.4	20.4	20.4		
June 10	Zero.....	1.7	1.65	1.6	1.65	18.87	0.1102
	Reading.....	20.5	20.6	20.5	20.52		

Mean depression, 0.110 mm. Molecular depression, 0.550 mm.

Experiment using 0.4 M KCl. Final observations as follows:

						Mean.	Deflect.	Depres.
Aug. 3	Zero.....	3.0	3.1	3.1	3.1	3.1	37.30	0.2175
	Reading..	40.3	40.4	40.5	40.3	40.4		
Aug. 6	Zero.....	2.4	2.4	2.3	2.3	2.35	37.22	0.2171
	Reading..	39.4	39.5	39.7	39.7	39.5		
	Zero.....	2.4	2.4	2.3	2.3	2.35	37.25	0.2172
	Reading..	39.5	39.7	39.6	39.6	39.6		
Aug. 7	Zero.....	1.9	1.8	2.0	2.0	1.94	37.36	0.2178
	Reading..	39.2	39.3	39.4	39.3	39.3		

Mean depression, 0.217 mm. Molecular depression, 0.542 mm.

1915. Experiment using 0.6 M KCl. Final observations as follows:

							Mean.	Deflect.	Depres.
June 9	Zero	1.4	1.4	1.5	1.5	1.25	1.4	56.65	0.3303
	Reading	58.0	50.0	58.1	58.1		58.05		
	Zero	1.6	1.6	1.5	1.7	1.5	1.57	56.43	0.329
	Reading	58.0	58.0	58.0			58.0		
June 10	Zero	1.65	1.65	1.80	1.6	1.6	1.66	56.45	0.3291
	Reading	58.2	58.0	58.1	58.15		58.1		
	Zero	1.7	1.6	1.65	1.7		1.65	56.48	0.3293
	Reading	58.1	58.15	58.2	58.1		58.13		

Mean depression, 0.329 mm. Molecular depression, 0.548 mm.

Experiment using 0.8 M KCl. Final observations as follows:

					Mean.	Deflect.	Depres.
July 15	Zero.....	1.2	1.3	1.3	1.27	75.23	0.4385
	Reading.....	76.5	76.5	76.5	76.5		
July 16	Zero.....	0.9	0.9	0.9	0.9	75.25	0.4386
	Reading.....	76.1	76.2	76.2	76.1		
	Zero.....	0.9	0.9	0.9	0.9	75.15	0.4381
	Reading.....	76.0	76.1	76.0	76.1		

Mean depression, 0.438 mm. Molecular depression, 0.547 mm.

1915. Experiment using 0.9 M KCl. Final observations as follows:

June 30	Zero.....	-1.65	-1.55	-1.60	(negative)	-1.60	84.65	0.4935
	Reading..	83.1	83.1	83.0	83.0	83.05		
July 2	Zero.....	2.2	2.2	2.25	2.30	2.25	84.51	0.4927
	Reading..	86.8	86.8	86.75	86.7	86.76		
July 8	Zero.....	1.8	1.9	2.0	2.0	1.92	84.68	0.4937
	Reading..	86.6	86.6	86.5	86.7	86.6		
July 9	Zero.....	2.0	2.1	2.0	2.1	2.05	84.65	0.4935
	Reading..	86.6	86.8	86.7	86.7	86.7		
July 16	Zero.....	0.9	0.9	0.9		0.9	84.65	0.4935
	Reading..	85.5	85.6	85.5	85.6	85.55		

Mean depression, 0.493 mm. Molecular depression, 0.548 mm.

1914. Experiment using 1.0 M KCl. Final observations as follows:

						Mean.	Deflect.	Depres.
Dec. 11	Zero.....	8.2	8.2	8.2		8.20	93.80	0.547
	Reading..	102.0	102.0	102.0		102.00		
	Zero.....	8.2	8.2	8.2		8.20	93.80	0.547
	Reading.....	102.0	102.0	102.0		102.00		
Dec. 12	Zero.....	8.1	8.1	8.2		8.13	93.74	0.5466
	Reading.....	101.9	101.9	101.8		101.87		
Dec. 16	Zero.....	8.8	8.8	8.8	8.7 8.9	8.80	93.80	0.547
	Reading.....	102.6	102.5	102.7		102.60		

Mean depression, 0.547 mm. Molecular depression, 0.547 mm.

Experiment using 1.2 M KCl. Final observation as follows:

Aug. 3	Zero.....	3.0	3.1	3.1	3.1	3.1	113.80	0.6634
	Reading...	117.0	116.9	116.9	116.85	116.9		
Aug. 4	Zero.....	2.8	2.9	3.0	2.9	2.9	113.73	0.6628
	Reading...	116.65	116.65	116.6	116.6	116.63		
Aug. 5	Zero.....	2.8	3.0	3.0	3.0	2.95	113.65	0.6625
	Reading...	116.6	116.5	116.6	116.8	116.6		
	Zero.....	2.9	3.0			2.95	113.65	0.6625
	Reading...	116.6	116.6	116.8	116.5	116.7		
Aug. 7	Zero.....	1.8	1.9	1.9	1.9	1.87	113.63	0.6623
	Reading...	115.5	115.5	115.5	115.5	115.5		

Mean depression, 0.663 mm. Molecular depression, 0.552 mm.

1915. Experiment using 1.5 M KCl. Final observations as follows:

					Mean	Deflect.	Depres.
Mar. 9	Zero.....	7.10	7.20	7.10	7.13	141.57	0.8255
	Reading	148.60	148.80	148.70	148.70		
Mar. 10	Zero.....	6.25	6.35	6.40	6.35	141.77	0.8267
	Reading	148.15	148.10	148.10	148.12		
	Zero.....	6.00	6.00	6.00	6.00		
	Reading	147.70	147.95	147.70	147.81		
Mar. 12	Zero.....	6.10	6.10	6.05	6.08	141.64	0.826
	Reading	147.70		147.65	147.72		
	Zero.....	7.00	7.05	7.10	7.05		
	Reading	148.60	148.70	148.85	148.66		
	*Zero.....	6.10	6.10	6.05	6.08		
	Reading	146.95	147.00	147.00	146.98		
	*Zero.....	7.00	7.05	7.10	7.05		
	Reading	148.00	147.90	148.00	147.97		
	Zero.....	7.10	7.05	7.20	7.10		
	Reading	148.40	148.45	148.50	148.46		
	Zero.....	6.30	6.30	6.30	6.30		
	Reading	147.95	147.80	147.75	147.85		
Mar. 16	Zero.....	6.95	7.00	6.95	6.97	141.55	0.8255
	Reading	148.50	148.65	148.65	148.61		
	Zero.....	6.15	6.20	6.15	6.17		
	Reading	147.90	147.90	147.85	147.88		
Mar. 17	Zero.....	6.90	6.90	6.95	6.92	141.71	0.8263
	Reading	148.45	148.60	148.50	148.50		
	Zero.....	6.05	6.10	6.05	6.07		
	Reading	147.75	147.65	147.85	147.75		
Mar. 18	Zero.....	6.80	6.80	6.85	6.82	141.68	0.8262
	Reading	148.30	148.35	148.40	148.37		
	Zero.....	6.05	6.10	6.05	6.07		
	Reading	147.65	147.75	147.80	147.73		
	Zero.....	6.80	6.80	6.85	6.82		
	Reading	148.40	148.35	148.35	148.37		
	Zero.....	6.05	6.10	6.05	6.07		
	Reading	147.65	147.75	147.80	147.73		

Mean depression, 0.826 mm. Molecular depression, 0.550 mm.

Experiment using 2.0 M KCl. Final observations as follows:

					Mean.	Deflect.	Depres.
Mar. 20	Zero.....	6.95	7.00	7.05	7.00	189.02	1.1018
	Reading.....	196.00	196.05	196.00	196.02		
Mar. 22	Zero.....	6.70	6.80	6.85	6.75	189.12	1.1023
	Reading....	195.85	195.90	195.95	195.90		
	Zero.....	6.35	6.30	6.40	6.35		
	Reading....	195.30	195.40	195.40	195.37		
	Zero.....	6.40	6.30	6.30	6.33		
	Reading....	195.20	195.25	195.20	195.22		

*These readings have been omitted in taking the mean, since it is apparent that the deviation is too great to admit of their being correct.

				Mean.	Deflect.	Depres.
Zero.....	6.90	7.00	6.90	6.93	189.02	1.1018
Reading....	196.00	195.95	195.90	195.95		
Zero.....	6.90	7.00	6.90	6.93	189.02	1.1018
Reading....	196.00	195.95	195.90	195.95		
Zero.....	6.40	6.30	6.30	6.33	188.95	1.1015
Reading....	195.30	195.30	195.25	195.28		
Zero.....	6.30	6.30	6.30	6.30	188.92	1.1013
Reading....	195.20	195.20	195.25	195.22		
Zero.....	7.00	6.95	7.00	6.98	188.95	1.1015
Reading....	195.90	195.90	195.90	195.90		

Mean depression, 1.1017 mm. Molecular depression, 0.551 mm.

TABULATION OF RESULTS, TEMPERATURE 20.0°.

Concentration. Mols KCl per 1000 g. H ₂ O.	Observed depression.	Molecular depression.
0.2	0.110	0.550
0.4	0.217	0.542
0.6	0.329	0.548
0.8	0.438	0.547
0.9	0.493	0.548
1.0	0.547	0.547
1.2	0.663	0.552
1.5	0.826	0.550
2.0	1.102	0.551

Summary.

(1) In the foregoing article the authors have described certain changes which have been made in the form of the apparatus since the publication of their original article, including (a): A thermostat, the temperature of which can be maintained constant to 0.001° for periods of twelve hours or more; (b) a simple mechanical device for continuous stirring of the solution and solvent while in vacuum, and (c) a more sensitive McLeod gauge for measuring the residual air pressure after the absorption of the water vapor.

(2) Actual observations of the vapor pressure lowering are made only after the McLeod gauge shows a residual air pressure of less than 0.0001 mm.

(3) Under these conditions the vapor pressure lowering of a given solution remains constant for days to 0.001 mm. as shown in the table of measurements above.

(4) Solutions of potassium chloride varying in concentration from 0.2 *M* to 2.0 *M* have been studied.

(5) It has been shown by the analysis of the solutions from the apparatus after the measurements have been made, that the change of concentration of the solutions during the process of removing the dissolved air and measuring the vapor tension lowerings is small enough to be neglected.

(6) The most striking feature of the experimental results is, that for all concentrations investigated, the molecular lowering of vapor tension is the same. Thus the lowering of a 0.2 *M* solution is 0.110 mm., while that of the 2.0 *M* solution is 1.1102 mm. Similar results have been obtained by Tower and Germann¹ from a study of the vapor tension of alcoholic solutions of potassium bromide and lithium chloride. Whether this phenomenon can be explained by the combination of the solvent and solute, as suggested by Tower and Germann, cannot be decided until the rigid applicability of Raoult's law has been tested with some non-electrolyte over the same range of concentration. This the authors purpose doing as soon as possible.

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THE EQUATION OF STATE FOR GASES AND LIQUIDS.

By F. H. MACDOUGALL.

Received October 6, 1915.

Van der Waals' equation, $(p + a/v^2)(v - b) = RT$, has for thirty years been accepted by chemists and physicists as a most valuable guide in the study of the behavior of gases and liquids. On the other hand, the limitations of the equation of the distinguished Hollander have also come to be generally recognized. From any two of the three quantities, critical temperature, critical pressure and critical volume, the theory of van der Waals enables us to calculate *a* and *b*. But if from the values of *a* and *b* so obtained, we calculate the third critical quantity, our result will be widely at variance with the facts. This is also evident when we remember that the theory of van der Waals requires that the critical density shall be 2.67 times that of an "ideal" gas under the same conditions of temperature and pressure, whereas in all cases hitherto investigated the ratio is much larger, usually about 3.7. Most of the modifications of the equation attempt to meet this condition of affairs, but are unable to raise the ratio above three.

Now there seems to be no doubt that the general ideas underlying the theory of van der Waals are of great value, enabling us to obtain a better insight into the nature of gases and liquids. It would seem to be worth while inquiring whether another method of deriving the equation of state is not theoretically sounder and more justifiable.

Van der Waals' method of applying a correction to the volume of the gas seems to be correct in principle, although the correction represented by the letter *b* may not be a "constant." Leaving out of account the surface layer of unknown thickness, the pressure throughout the fluid should undoubtedly be represented by the expression $RT/v - b$. Owing, however, to unbalanced molecular forces in the surface layer directed to-

¹ THIS JOURNAL, 36, 2449 (1914).

wards the interior, the external pressure will be less than $RT/v - b$ by the pressure due to the unbalanced molecular forces. Van der Waals assumes this molecular pressure to be represented by a/v^2 and thus obtains his equation

$$p = \frac{RT}{v - b} - \frac{a}{v^2}.$$

Now it may well be that in order to obtain the external pressure, we should, instead of subtracting a term from $RT/v - b$, multiply it by a function, which will of course always be less than unity. This is the result that Dieterici¹ has obtained, and I shall indicate as briefly as possible his method of reasoning.

In the interior of a fluid the attractive forces between the molecules are balanced; only near the surface are the molecules subject to an unbalanced force directed towards the interior. Molecules with sufficiently low velocities moving towards the surface will be unable to reach it, while all molecules moving from the surface towards the interior will be assisted by the force directed inward. The result will be that the density of the surface layer will decrease from the interior towards the surface, where its value will depend on the external pressure. Only molecules having a velocity greater than a certain value will be able to penetrate this inhomogeneous layer and exert a pressure on the walls of the containing vessel. If we can determine what fraction of the total number of molecules has a velocity greater than a fixed value, then the external pressure (p) will be that fraction of the pressure in the interior, $RT/v - b$. Now if α be the most probable speed, and s be the speed a molecule must possess in order to be able just to penetrate to the surface, then the fraction we are considering is calculated to be e^{-s^2/α^2} , where e is the base of the natural logarithms. If we introduce the speed c , the square root of the mean of the squares of the speeds, we have $c^2 = \frac{3}{2}\alpha^2$ and our fraction becomes $e^{-\frac{1}{3} \frac{s^2}{c^2}}$. If m be the mass of a molecule and n the number of molecules, the expression may be written $e^{-\frac{1}{3} \frac{nm s^2}{RT}} = e^{-\frac{1}{2} \frac{nm s^2}{RT}}$. Now $\frac{1}{2} nm s^2$ is the work done by a molecule against the molecular forces in reaching the wall; we can therefore write the following equation:

$$p = \frac{RT}{v - b} e^{-A/RT} \quad (1)$$

where A is a measure of the work done by the molecules in penetrating to the surface. If now we make an assumption as to how A depends on the volume, we shall obtain an equation of state. Dieterici assumes that A is proportional to the density or $A = a/v$ and thus obtains the Dieterici equation of state

¹ *Ann. Physik. u. Chem.*, 11, 700 (1899).

$$p = \frac{RT}{v-b} e^{-a/vRT}. \quad (2)$$

The object of this paper may be said to be to study this equation in detail and to apply it to a number of well-investigated substances. The results obtained seem worthy of consideration. Dieterici himself showed that his equation reproduces the critical state very well, and in particular gives 3.695 as the value of the ratio $RT_c/p_c v_c$, in close agreement with the actual results obtained by Young and others. As far as I can learn from the available literature, Dieterici did not get much farther and has not persuaded chemists and physicists to adopt his form of the equation of state. One great difficulty in testing the equation lies in the fact that the "constants" a and b are really variables. This has been generally recognized in recent years and the view has been expressed that they are both temperature and volume functions. I hope to show that they are mainly functions of the temperature and that their variation with change in volume is probably small.

Before proceeding to study Dieterici's equation further, it might be well to show its relation to the original one of van der Waals. Dieterici's equation can be written, when the volume v is large as compared with b in the form

$$p = \frac{RT}{v-b} \left(1 - \frac{a}{vRT} \right) = \frac{RT}{v-b} - \frac{a}{v(v-b)},$$

which is virtually identical with the van der Waals $p = RT/(v-b) - a/v^2$. It is evident then that all the results obtainable from the van der Waals equation will be deducible from the Dieterici equation when only low pressures are considered. When a gas is under high pressure and, in particular, when the gas is in the critical state, the two equations will differ considerably. And it is to be noted that it is just here that the van der Waals equation loses its validity, while the Dieterici equation reproduces the critical results in most cases with accuracy.

Critical State.

The values of p , v , and T at the critical state in terms of a , b and R are obtained by putting $(dp/dv)_T = 0$ and $(d^2p/dv^2)_T = 0$. If we plot the Dieterici equation having the pressures as ordinates and the volumes as abscissae, we shall get for different values of T the isothermal curves. The geometrical interpretation of $(dp/dv)_T = 0$ is that, when this condition holds, we have a horizontal tangent; that is, the curve has at this point a maximum or minimum value or a point of inflexion. If the second derivative also vanishes for the same values of v , the point is a point of inflexion. And that is the critical point. Assuming that a and b are independent of the volume, we obtain the following results:

$$\left(\frac{p}{T}\right)_T = -e^{-a/vRT} \frac{(RTv^2 - av + ab)}{v^2(v-b)^2} = -\frac{p}{v-b} \left(1 - \frac{a(v-b)}{v^2RT}\right) \quad (3)$$

$$\left(\frac{p}{T}\right)_T = e^{-a/vRT} \left[\frac{2RT}{(v-b)^2} + \frac{a^2}{RTv^4(v-b)} - \frac{2a}{v^2(v-b)} - \frac{2a}{v^2(v-b)^2} \right] \quad (4)$$

Now $(dp/dv)_T$ will vanish when v is infinitely great, a value which does not concern us here; when v is equal to zero, which is a physically impossible value since v cannot be less than b ; and finally when $RTv^2 - av + ab = 0$. From this equation we obtain

$$v = \frac{a \pm \sqrt{a^2 - 4abRT}}{2RT} \quad (5)$$

the result shows us that there are always two horizontal tangents, real and imaginary or coincident. The two tangents coincide at the critical point and Equation 5 tells us that at this point $a^2 - 4abRT = 0$. At the critical point, $a = 4bRT_c$ and therefore the critical temperature T_c is equal to $a/4bR$; at the same time, from Equation 5 we find that the critical volume v_c is equal to $a/2RT_c$ and therefore equal to $2b$. Substituting these values in the Dieterici equation of state, we obtain

$$p_c = \frac{RT_c}{e^2b} = \frac{2RT_c}{e^2v_c} = \frac{a}{4e^2b^2} = \frac{a}{29.56b^2}$$

$$2RT_c/p_c v_c = e^2/2 = 3.695.$$

These results could of course have been obtained by combining $(p/T)_T = 0$ with $(d^2p/dv^2)_T = 0$, but the method adopted is somewhat simpler. In any case, one can easily satisfy himself that the values obtained for v_c and T_c will make both derivatives vanish.

It may be interesting to compare these results with those derived from the original van der Waals equation.

Van der Waals.	Dieterici.	
$v_c = 3b$	$v_c = 2b$	} (6)
$T_c = 8a/27Rb$	$T_c = a/4Rb$	
$p_c = a/27b^2$	$p_c = a/4e^2b^2 = a/29.56b^2$	

that the isothermals as given by the Dieterici equation will have the same general appearance as those given by that of van der Waals will be evident if we consider that the condition for a horizontal tangent is given by Equation 5. At the critical temperature the two values of v coincide; above this temperature, $a^2 - 4abRT$ is negative, the two values become imaginary; that is, there is no horizontal tangent. Below the critical temperature, however, there are two real and unequal values

of v , corresponding to each of which there is a horizontal tangent on the theoretical isothermal. In other words, the isothermal curve has a maximum and a minimum value. For certain values of p , then, horizontal lines may be drawn cutting the isothermal curve in three points, giving three values of v corresponding to the same pressure. It is clear then that the theoretical isothermals as given by the Dieterici equation are quite similar in their general appearance to those of van der Waals.

The following results are set down here, partly for reference, partly so that they may be compared with the well-known deductions from the equation of van der Waals:

$$p = \frac{RT}{v-b} e^{-a/vRT} \quad (2)$$

$$\left(\frac{dp}{dv}\right)_T = -\frac{e^{-a/vRT}}{v^2(v-b)^2} (RTv^2 - av + ab) = -\frac{p}{v-b} \left[1 - \frac{a(v-b)}{v^2RT}\right] \quad (3)$$

$$\left(\frac{dp}{dT}\right)_v = \frac{R}{v-b} \left(1 + \frac{a}{vRT}\right) e^{-a/vRT} = \frac{p}{T} \left(1 + \frac{a}{vRT}\right) \quad (7)$$

$$\left(\frac{dv}{dT}\right)_p = \frac{v-b}{T} \left(\frac{1 + a/vRT}{1 - a(v-b)/v^2RT}\right) = \frac{R}{p} \cdot e^{-a/vRT} \cdot \frac{(1 + a/vRT)}{1 - a(v-b)/v^2RT} \quad (8)$$

Where u represents the energy of the gas,

$$\left(\frac{du}{dv}\right)_T = T \left(\frac{dp}{dT}\right)_v - p = \frac{ap}{vRT} = \frac{a e^{-a/vRT}}{v(v-b)} = \frac{a}{v^2} \text{ (approx.)} \quad (9)$$

$$C_p = C_v + R e^{-a/vRT} \frac{(1 + a/vRT)^2}{1 - a(v-b)/v^2RT} = C_v + R + \frac{2a}{vT} \text{ (approx.)} \quad (10)$$

Assuming a and b to be functions of T ,

$$\left(\frac{dp}{dT}\right)_v = \frac{p}{T} \left[1 + \frac{a}{vRT} + \frac{T}{v-b} \cdot \frac{db}{dT} - \frac{1}{Rv} \cdot \frac{da}{dT}\right]. \quad 7(a)$$

The value of the product pv at constant temperature varies with the pressure p . The law governing this relation can be deduced from the Dieterici equation and is as follows:

$$\left(\frac{d(pv)}{dp}\right)_T = \frac{v^2(bRT - a) + abv}{v^2RT - av + ab} \quad (11)$$

This expression is positive when $bRT > a$, or $b > a/RT$, as must be the case with hydrogen at ordinary temperatures and even at as low a temperature as -147° . If, however, a/RT is greater than b , the expression is at first negative for small values of p , becomes equal to zero and finally

positive when p is sufficiently increased or v sufficiently diminished. When the expression becomes zero, we have a minimum value of pv . The condition for this minimum is obtained by putting $v^2(bRT - a) + abv$ equal to zero. Neglecting the impossible value, $v = 0$, we arrive at the following relations which hold when pv has its minimum value:

$$v = ab/(a - bRT) \quad (12)$$

$$pv_{(\min.)} = \frac{a}{b} e^{1 - a/bRT} \quad (13)$$

$$p = \frac{a - bRT}{b^2} e^{1 - a/bRT} \quad (14)$$

Equations 12, 13 and 14 can be used in calculating the values of a and b , above the critical temperature.

When a is greater than bRT , as we have seen, pv at first diminishes as p increases; when a is less than bRT , pv increases with p . When $a = bRT$, i. e., when $T = a/Rb$, the minimum pv would occur when $v = \text{infinity}$ and $p = 0$; in other words, at this temperature the minimum just fails to appear and the pv curve would be a horizontal straight line for a short distance. Under these conditions, the gas would follow Boyle's law with great accuracy. If a and b were independent of the temperature, we should be able to calculate the temperature at which a gas would obey Boyle's law accurately as equal to four times the critical temperature. Since a and b are functions of the temperature, the temperature calculated in this manner will be usually quite in error. In cases where this temperature is known accurately for any gas, we have a means of finding the value of the ratio a/b at this temperature, for the relation $a = bRT$ may be written

$$a/b = RT. \quad (15)$$

As an example, Young, on page 34 of his "Stoichiometry" states that at about 52° , $d(pv)/dp$ for nitrogen is equal to zero. Accordingly at this temperature, the ratio $a/b = 325/273 = 1.19$, when the unit mass of nitrogen is that which occupies unit volume at zero, and a pressure of one atmosphere.

Equation 11 can be simplified for the case that the pressures obtaining are small and the volumes large. We obtain, then,

$$\frac{d(pv)}{dp} = \frac{v^2(bRT - a)}{v^2RT} = b - \frac{a}{RT}$$

or

$$\frac{p_2 v_2 - p_1 v_1}{p_2 - p_1} = b - \frac{a}{RT}. \quad (16)$$

This equation may also be obtained directly from the Dieterici equation, which for low pressures may be written, $pv = RT + pb - a/v$.

Hence $p_2v_2 - p_1v_1 = (p_2 - p_1)b - (1/v_2 - 1/v_1)a = (p_2 - p_1)(b - a/RT)$ and finally Equation 16.

PV Curve at the Critical Temperature.

Some interesting results are obtained by applying Equations 12, 13 and 14 when the gas is at the critical temperature. In this case, when pv has its minimum value, the following relations hold:

$$\left. \begin{aligned} v &= \frac{1}{3}b = \frac{2}{3}v_c \\ p &= 3a/4e^3b^2 = 3/e p_c = 1.104 p_c \\ pv_{\min.} &= a/e^3b = 2/e p_c v_c = 4/e^3 RT_c = 0.736 p_c v_c = 0.1991 RT_c \end{aligned} \right\} \quad (17)$$

The above results may be expressed in words as follows: At the critical temperature, the minimum value of pv is about $3/4$ of its value in the critical state, and about $1/e$ of its "theoretical" value; the corresponding volume is $2/3$ of the critical volume, and the corresponding pressure is about 10% greater than the critical pressure. It might also be added that Dieterici's equation for the critical isothermal becomes

$$p = a/4b(v - b) e^{-4b/v} \quad (18)$$

which for low pressures is equivalent to

$$p(v + 3b) = RT_c.$$

Negative Pressures Impossible.

Returning to a consideration of Equation 5, we said that the two values of v given by this equation correspond to the maximum and minimum pressures on any theoretical isothermal. As is well known, on using van der Waals' equation, the theoretical minimum pressure is frequently negative, since the term a/v^2 may easily become greater than the term $RT/(v - b)$. Using the Dieterici equation, the external pressure (for that is what p refers to) becomes zero only at the absolute zero of temperature and under no circumstances becomes negative. Young,¹ describes an experiment by Worthington,² in which a sealed tube completely full of a pure liquid is cooled slowly. He finds that in some experiments the thick-walled tube actually collapsed owing to what he calls the enormous tension. Now on both van der Waals' theory and on that of Dieterici, it is assumed that there is no attractive force between the molecules of the fluid and the wall. The only force assumed at the boundary is that due to the bombardment of the wall by the molecules which reach the surface. The hydrostatic pressure may be here neglected. In the absence of any adhesive force between the fluid and the wall, a negative external pressure is inconceivable. For, assume that under given conditions, the pressure directed towards the interior and due to molecular attraction is equal to p_0 . The pressure on any imaginary unit area in the interior will still be given

¹ "Stoichiometry," 1908, p. 205.

² *Phil. Trans.*, (A) 183, 355 (1892).

by $RT/(v-b)$. Van der Waals' equation requires us to imagine that under certain circumstances p_0 is greater than $RT/(v-b)$. What would be the result? The result would be that more molecules would move from the surface layers to the interior than in the opposite direction. This would mean that the volume of the fluid would decrease until $RT/(v-b)$ became greater than p , since $RT/(v-b)$ must be greater than p_0 in order that the number of molecules moving in the two directions shall be equal. For molecules moving towards the surface layer have to overcome a force, while those moving into the interior from the surface are moving in the same direction as the force. The phenomena described by Worthington then cannot be explained on the fundamental assumptions either of van der Waals or of Dieterici which do not consider any attractive forces between the fluid and the wall.

Maximum and Minimum Pressures.

We obtain the theoretical maximum and minimum pressures on any isothermal curve by substituting in the Dieterici equation the two values of v from Equation 5. Thus:

$$p_{\max.} = \frac{2R^*T^2}{a - bRT + \sqrt{a^2 - 4abRT}} e^{-\frac{2a}{a + \sqrt{a^2 - 4abRT}}} \quad (19a)$$

$$p_{\min.} = \frac{2R^*T^2}{a - bRT - \sqrt{a^2 - 4abRT}} e^{-\frac{2a}{a - \sqrt{a^2 - 4abRT}}} \quad (19b)$$

Also

$$p_{\max.} \times p_{\min.} = \frac{R^*T^2}{b^2} e^{-a/bRT}$$

and therefore

$$\sqrt{p_{\max.} \times p_{\min.}} = \frac{RT}{b} e^{-a/2bRT} \quad (19c)$$

According to Equation 19c, the geometric mean of the maximum and minimum pressure on any isothermal is the pressure corresponding to the volume $2b$. At the critical temperature, this volume would be the critical volume and the pressure, the critical pressure. At a lower temperature, the value of $2b$ will be different from the critical volume, since we shall see that b is a function of the temperature. We shall now proceed to discuss a method of determining the value of b at different temperatures.

Determination of b at Different Temperatures.

If a substance is at a temperature lower than its critical temperature, experience teaches us that a certain portion of the theoretical isothermal curve is not realizable. Instead of the pressure increasing to a maximum, falling to a minimum and then increasing indefinitely as the volume is decreased, the pressure increases to a certain value and then remains constant until

the gas is completely condensed into liquid. If this line of constant pressure be drawn in our pv diagram, it will cut the theoretical isothermal in three points; and we know from thermodynamics that the two areas bounded by the isothermal and the horizontal line, one above this line and the other under it, are equal. Two of the points correspond to the volumes of the liquid and the saturated vapor, the third point on our continuous isothermal corresponds in practice to a state in which both liquid and vapor are present. Let v_1 , v_2 and v_3 represent the volumes of the liquid, vapor and the third intermediate volume, all corresponding to the pressure of the saturated vapor. We have then the equations

$$p_s = \frac{RT}{v_1 - b} e^{-\frac{a}{nRT}} = \frac{RT}{v_2 - b} e^{-\frac{a}{nRT}} = \frac{RT}{v_3 - b} e^{-\frac{a}{nRT}}. \quad (20)$$

Evidently the product of the second and third expressions is equal to the square of the fourth. We thus obtain

$$\frac{1}{(v_1 - b)(v_2 - b)} e^{-\frac{a}{RT} \left(\frac{1}{v_1} + \frac{1}{v_2} \right)} = \frac{1}{(v_3 - b)^2} e^{-\frac{a}{RT} \cdot \frac{2}{v_3}}.$$

Now if we make the assumption that $1/v_1 + 1/v_2 = 2/v_3$, then, of course, $(v_1 - b)(v_2 - b) = (v_3 - b)^2$. From these two relations the following results are easily deduced:

$$v_3 = 2b \quad (21a)$$

$$1/b = 1/v_1 + 1/v_2 \quad (21b)$$

$$v_1 = \frac{bv_2}{v_2 - b}; \quad v_2 = \frac{bv_1}{v_1 - b} \quad (21c)$$

$$\frac{v_2}{v_1} = \frac{v_2 - b}{b} = \frac{b}{v_1 - b} \quad (21d)$$

$$\left(\frac{v_2}{v_1} \right)^2 = \frac{v_2 - b}{v_1 - b} \quad (21e)$$

And finally, for the pressure at which liquid and vapor are in equilibrium, since $v_3 = 2b$, we obtain

$$p_s = \frac{RT}{b} e^{-\frac{a}{2bRT}}. \quad (22)$$

Comparing Equations 22 with 19c, we see that the pressure at which liquid and vapor are in equilibrium at any temperature is equal to the geometric mean of the maximum and minimum pressures on the theoretical isothermal for that temperature. Making use of Equation 21b, and letting d_1 and d_2 stand for the densities of liquid and saturated vapor, Equation 22 may be written as follows:

$$p_s = \left(\frac{1}{v_1} + \frac{1}{v_2} \right) RT \cdot e^{-\frac{a}{2RT} \left(\frac{1}{v_1} + \frac{1}{v_2} \right)} \quad (23)$$

$$p_s = (d_1 + d_2) RT \cdot e^{-\frac{a(d_1 + d_2)}{2RT}} \quad (24)$$

The above results have been obtained on the assumption that $2/v_3 = 1/v_1 + 1/v_2$. Any of the equations numbered 21 would of course be an equivalent assumption, such as, for example, that $v_3 = 2b$. Our assumption may also be written in the form $d_3 = (d_1 + d_2)/2$, i. e., the third point on the theoretical isothermal cut by the line of constant pressure would represent a density which is the arithmetic mean of the densities of liquid and the saturated vapor. Now what grounds are there for this assumption? In the first place, at the critical temperature, v_1 , v_2 and v_3 are all equal to $2b = v_c$. As the temperature is decreased, v_1 decreases fairly rapidly and v_2 increases quite rapidly, while the intermediate volume, v_3 , might be expected to change very slowly. And in fact, if a p - v diagram containing a number of isothermals below the critical temperature be examined, it will be seen that the point where the line of constant pressure cuts the descending portion of the isothermal represents a volume which does not differ much from the critical volume; that is, v_3 does not differ very much, as the temperature decreases, from $v_c = 2b_c$, where b_c is the value of b at the critical temperature. It seemed very plausible to assume that v_3 is equal to $2b$ at every temperature, although not necessarily equal to $2b_c$.

Another circumstance which led me to the assumption that $2/v_3 = 1/v_1 + 1/v_2$ was a consideration of the law of Cailletet and Mathias,¹ according to which the mean of the densities of liquid and saturated vapor is a linear function of the temperature, a statement therefore which would hold for d_3 or $(d_1 + d_2)/2$. Expressed in our symbols, then, $d_3 = d_c + \alpha T$, where α is always very small. The fact that $(d_1 + d_2)/2$ is so nearly constant, varying only slightly and uniformly with the temperature seemed to me to be of great significance. If the mean of the densities of liquid and saturated vapor is given by such a simple relation, it seemed plausible to assume that this mean is identical with that given by the third point on the theoretical isothermal. Additional support to the assumption is given by the fact that we found the geometric mean of the maximum and minimum pressures on any theoretical isothermal to be equal to $\frac{RT}{b} e^{-\frac{a}{2bRT}}$ (cf. Equation 19c). Now this is exactly

the same pressure which we calculate to be the pressure of saturated vapor, when we assume that $v_3 = 2b$. It seems fair to assume that this result is not simply a chance mathematical agreement, but that it corresponds to some physical reality. However insufficient the grounds for this assumption may be, I have adopted it in this paper.

Young² has shown that in the equation representing the law of Cailletet and Mathias, which may be written in the form $s_T = s_0 + \alpha T$, the value

¹ *Compt. rend.*, 102, 1202 (1886).

² "Stoichiometry," p. 228.

of $(-\alpha T_c/s_c)$ is approximately unity for a large number of substances. In this equation, $s_T = (d_1 + d_2)/2$ and s_c is the critical density, and s_0 would be equal to half the density of the liquid at absolute zero, since at this temperature the density of the vapor would be zero. If the law of Cailletet and Mathias is assumed to hold accurately down to absolute zero and if the value of $(-\alpha T_c/s_c)$ is exactly unity, one can easily deduce that at the absolute zero, the density of a substance would be four times the critical density. Again, since $s_T = (d_1 + d_2)/2 = 1/2b$, we can obtain the following result:

$$b_T = \frac{b_c}{(2 - T/T_c)} \quad (25)$$

This result holds only for those substances for which the law of Cailletet and Mathias is valid and for which $(-\alpha T_c/s_c)$ is approximately unity.

It might be added that Thorpe and Rücker's formula¹ for estimating the critical temperature is easily deducible, if we assume the law of Cailletet and Mathias and that $(-\alpha T_c/s_c)$ is approximately unity. For if d_1 and d_2 now represent the densities of a liquid at the two temperatures T_1 and T_2 , sufficiently below the critical temperature, the densities of saturated vapor may be neglected and we obtain $d_1 = 2s_{T_1}$. Accordingly $d_1 = 2s_c(2 - T_1/T_c)$ and $d_2 = 2s_c(2 - T_2/T_c)$, from which we easily obtain

$$\frac{T_2 d_1 - T_1 d_2}{2(d_1 - d_2)} = T_c.$$

Now Thorpe and Rücker's formula is

$$T_c = \frac{T_2 d_1 - T_1 d_2}{A(d_1 - d_2)},$$

where A varies from 1.926 to 2.030 for 24 substances with a mean value of 1.974.

Determination of a .

From the relation

$$p_s = \frac{RT}{v_1 - b} e^{-\frac{a}{v_1 RT}} = \frac{RT}{v_2 - b} e^{-\frac{a}{v_2 RT}}$$

we obtain

$$a_1 = \frac{v_1 v_2}{v_2 - v_1} RT \log_e \frac{v_2 - b}{v_1 - b},$$

or since, according to Equation 21e, $(v_2 - b)/(v_1 - b) = (v_2/v_1)^2$,

$$a_1 = \frac{2v_1 v_2}{v_2 - v_1} RT \log_e \frac{v_2}{v_1}. \quad (26)$$

Expressed in terms of the densities d_1 and d_2 , Equation 26 becomes

¹ Quoted in Young's "Stoichiometry," p. 183.

$$a_1 = \frac{2RT}{d_1 - d_2} \log_e \frac{d_1}{d_2}. \quad (26a)$$

I have called the " a " of Equations 26 and 26a, a_1 , since a can be calculated in several other ways. From the set of Equations 20, we obtain the following (since $v_2 = 2b$):

$$a_2 = 2bRT \log_e RT/pb \quad (27)$$

$$a_3 = v_1 RT \log_e RT/p(v_1 - b) \quad (28)$$

$$a_4 = v_2 RT \log_e RT/p(v_2 - b) \quad (29)$$

An investigation of Equations 26–29 will show that Equation 29 is likely to be the least accurate. In the first place $p(v_2 - b)$ is very nearly equal to RT , so that the logarithm of their quotient, which is the same as the difference of their logarithms, will be greatly affected by small errors in the assumed values of p and v_2 . As regards an error in the value of p , its effect on a_4 will be v_2/v_1 times as great as on a_3 . Then there is no doubt that usually v_1 is determined more accurately than v_2 .

Another method which I have used in calculating a and b for hydrogen is based on Equation 7 or 7a. By Equation 7

$$1 + \frac{a}{vRT} = \frac{dp/dT}{p/T} = \frac{Tdp}{pdT} = \frac{d \log p}{d \log T}. \quad (30)$$

If the variation of a and b with the temperature be taken into account, we have

$$1 + \frac{a}{vRT} + \frac{T}{v-b} \frac{dh}{dT} - \frac{1}{vR} \frac{da}{dT} = \frac{d \log p}{d \log T}. \quad (30a)$$

If in any particular case, a and b are independent of the temperature, or if the expression $\left(\frac{T}{v-b} \frac{db}{dT} - \frac{1}{vR} \frac{da}{dT} \right)$ is equal to zero, then the simpler Equation 30 may be employed in determining a , and hence b .

Latent Heat of Vaporization.

In order to determine the latent heat of vaporization, we must calculate the work that is done when the liquid expands isothermally from the volume v_1 to the volume v_2 . This takes place in practice under the constant external pressure of saturated vapor, p_s . The same work will be done if the expansion is supposed to follow the course of the theoretical isothermal curve. The total work will be expressed by the definite integral

$$L = \int_{v_1}^{v_2} \frac{RT}{v-b} \cdot dv = RT \log_e \frac{v_2 - b}{v_1 - b} = 2RT \log_e \frac{v_2}{v_1}, \quad (31)$$

if we make use of Equation 21c. $RT/(v-b)$ represents the pressure throughout the fluid except in the surface layer which is negligible. Accordingly $\frac{RT}{v-b} dv$ represents the total work done when the volume

increases by the increment dv . Equation 31 includes the external work, the amount of which is $p(v_2 - v_1)$. Hence the internal heat of vaporization would be

$$I = 2RT \log_e \frac{v_2}{v_1} - p(v_2 - v_1). \quad (31a)$$

Comparing Equation 31 with Equation 26, we see that we may write

$$L = 2RT \log_e \frac{v_2}{v_1} = \frac{a}{v_1} - \frac{a}{v_2}. \quad (32)$$

The expression $a/v_1 - a/v_2$ is accordingly a measure of the total heat of vaporization, whereas according to the theory of van der Waals it measures the internal heat of vaporization only. Equation 32 agrees with the assumption made by Dieterici in deriving his original equation that the work done by the molecules in penetrating the surface layer is equal to a/v . According to Kendall,¹ Dieterici has proposed a formula, $I = cRT \log v_2/v_1$ for the internal heat of vaporization. I have not yet been able to obtain a copy of the article in which this formula is deduced; it is, however, to be noted that it is Dieterici's formula for the internal heat of vaporization which is similar to mine for the total effect.

Joule-Thomson Effect.

Our methods of arriving at values of a and b may be summarized as follows: At the critical temperature, a and b can be calculated from the critical data according to equations numbered 6. Above the critical temperature, so long as pv still has a minimum value, use may be made of Equations 12, 13 and 14. Below the critical temperature, Equations 21b and 26 to 29 are to be employed. And of course Equations 30 and 30a are valid at all temperatures and can be used where the data are sufficiently accurate. Another method of finding a relationship between a and b is based on the Joule-Thomson effect. If ΔT be the change in temperature, Δp the change in pressure, in the Joule-Thomson experiments, we have the following relation:²

$$\Delta T = \frac{T(dv/dT)_p - v}{c_p} \cdot \Delta p \quad (33)$$

If we substitute for $(dv/dT)_p$, the value given by Equation 8, we obtain the following approximate result:

$$\Delta T = \frac{2a/RT - b}{c_p} \cdot \Delta p \quad (34)$$

Equation 34 will hold most accurately when only low pressures are employed. It is identical with the formula derived by van der Waals from his original equation, as we should expect. If the ratio $\Delta T/\Delta p$ is de-

¹ THIS JOURNAL, 36, 1620 (1914).

² Planck, "Thermodynamik," 1905, p. 123.

terminated accurately at any temperature, we have a means of calculating $2a/RT - b$; while by using Equation 16 we can obtain the value of $b - a/RT$. Hence we can find a and b . Further discussion of these points will appear when we apply our equations to the experimental results.

Applications.

In this paper I have taken -273.09°C. as the absolute zero of temperature and 22412 cc. as the volume of a gram-molecule of an ideal gas under the pressure of one atmosphere.¹ The value assumed for the constant R for a mol is 62372 when a mm. of mercury is the unit of pressure, 82.07 when the unit of pressure is one atmosphere. The unit of volume is always one cubic centimeter. When the equations apply to a mass of gas whose volume is considered to be unity when the pressure is one atmosphere and the temperature is 0°C. , the value of R is approximately $1/273$.

Isopentane.—Tables I and II contain the results of applying our equations to isopentane. The data for the specific volumes of liquid and saturated vapor are by Young as given in Landolt-Börnstein's *Tabellen*.² The observed pressures are also by Young and are taken from an article by Dieterici.³ The results refer to 1 g. of the substance; pressures are given in millimeters of mercury. Accordingly the value of the constant R is $62372/72.09$. The orthobaric volumes of liquid and vapor are represented by v_1 and v_2 , respectively; b is calculated using Equation 21b, and a_1, a_2, a_3 , and a_4 by means of Equations 26 to 29.

TABLE I.—ISOPENTANE; UNIT MASS = 1 g.

$t^\circ \text{C.}$	v_1 cc.	v_2 cc.	b cc.	$a_1 \times 10^{-4}$	$a_2 \times 10^{-4}$	$a_3 \times 10^{-4}$	$a_4 \times 10^{-4}$
0	1.5642	909	1.5615	4.713	4.704	4.708	2.223
20	1.6140	426.6	1.6079	4.583	4.582	4.582	4.450
40	1.6700	224.4	1.6577	4.461	4.466	4.467	4.434
60	1.7334	127.6	1.7102	4.354	4.353	4.354	4.310
80	1.8051	77.700	1.7641	4.248	4.236	4.242	3.987
100	1.8947	49.505	1.8248	4.150	4.120	4.135	3.747
110	1.9455	39.793	1.8548	4.093	4.059	4.075	3.727
120	2.0036	32.196	1.8862	4.036	3.991	4.012	3.650
130	2.0721	26.103	1.9197	3.977	3.922	3.948	3.604
140	2.1542	21.151	1.9551	3.916	3.860	3.881	3.564
150	2.2497	17.141	1.9887	3.850	3.771	3.806	3.512
160	2.3776	13.719	2.0264	3.778	3.690	3.726	3.480
170	2.5549	10.710	2.0628	3.687	3.599	3.633	3.459
180	2.8588	7.9491	2.1026	3.579	3.503	3.528	3.436
183	3.0202	7.0522	2.1146	3.535	3.473	3.491	3.432
186	3.3025	5.9666	2.1258	3.476	3.441	3.449	3.428
187.8	4.2680	4.2680	2.1340	3.404	3.423	3.423	3.423

¹ Young, "Stoichiometry," 1908, p. 39.

² 1912, p. 158.

³ *Ann. Physik*, 9, 176 (1903).

TABLE II.—ISOPENTANE; UNIT MASS = 1 g.

t° C.	p (obs.).	$p = \frac{RT}{b} e^{-\frac{a_1}{2bRT}}$	% error.	$a_1 \times b \times 10^{-4}$	L (calc.).	L (Young).
0	257.7	254.7	1.2	7.35	95.8	86.8
20	572.6	571.9	0.1	7.36	90.0	82.9
40	1131	1134	0.3	7.40	84.5	78.8
60	2036	2034	0.1	7.45	78.9	74.4
80	3401	3364	1.1	7.50	73.2	69.8
100	5355	5222	2.5	7.58	67.1	64.6
110	6586	6406	2.7	7.59	63.7	61.7
120	8040	7762	3.4	7.62	60.1	58.5
130	9707	9317	4.0	7.63	56.2	54.8
140	11620	11091	4.5	7.65	52.0	50.7
150	13804	13080	5.2	7.66	47.3	46.5
160	16285	15369	5.6	7.65	41.8	41.0
170	19094	18061	5.4	7.61	35.0	34.2
180	22262	21259	4.5	7.53	25.5	24.5
183	23288	22434	3.7	7.47	21.3	20.2
186	24350	23862	2.0	7.38	15.0	13.9
187.8	25005	25287	1.1	7.26	0	0

A study of Table I shows that the value of a decreases from about 4.7×10^6 at 0°C. to 3.4×10^6 at 187.8°C. , the critical temperature. The values of a_1 , a_2 and a_3 agree very well throughout, whereas in the case of a_4 , its values near 0° and near the critical temperature agree with those of a_1 , a_2 and a_3 , but at intermediate temperatures, a_4 is considerably less than a_1 , a_2 and a_3 . I am not able wholly to account for this divergence, although there is no doubt that some of the discrepancy may be due to errors in the assumed values of p and v_3 . As has been previously remarked, an error in the value of p would have greater effect on the calculated value of a_4 than on that of a_3 or a_2 . Note that a_1 is calculated without any use of the value of p . Its value is determined entirely by v_1 , v_2 and T . In Table II the values of p at the different temperatures have been calculated, using Equation 22 and a_1 . The column is headed $p = \frac{RT}{b} e^{-\frac{a_1}{2bRT}}$, but exactly the same values are obtained when we use the equations

$$p = \frac{RT}{v_1 - b} e^{-\frac{a_1}{v_1 RT}} \quad \text{or} \quad p = \frac{RT}{v_2 - b} e^{-\frac{a_1}{v_2 RT}}.$$

It is to be noted that we should of course obtain the observed values of p , if instead of a_1 we had used a_2 , a_3 , or a_4 in the corresponding equations. Since a_2 and a_3 do not differ very much from a_1 , it is evident that a small error in the value of a will seriously affect the calculated values of p , except when the equation $p = \frac{RT}{v_2 - b} e^{-\frac{a}{v_2 RT}}$ is used to calculate p , in which case a considerable error in a produces only a small change in p .

If we compare the calculated with the experimental values of p , we notice that the maximum error amounts to 5.6% at about 30° below the critical temperature. This error is, of course, considerable, but still hardly sufficient to invalidate the views here presented or to render them unworthy of discussion.

In Column 5 of Table II are given the values of the product $ab \times 10^{-4}$, and it will be at once evident that this product exhibits a noteworthy constancy throughout the whole temperature interval studied. Now for the two dozen or so substances which Young has investigated and for which he found $(-aT_c/s_c)$ to be nearly equal to unity, we deduced Equation 25, viz., $b_T = b_c/(2 - T/T_c)$. If the product ab be supposed to be absolutely constant, we should have

$$a_T = a_c(2 - T/T_c). \quad (25a)$$

It must be clearly borne in mind that these results are supposed to hold only under the stated conditions and only below the critical temperature. Applied above this temperature, Equations 25 and 25a would lead to results which are contrary to all experimental evidence. For at a temperature equal to twice the critical, b would become infinity and a would vanish.

In Column 6 of Table II are given the results obtained for the heat of vaporization of one gram of isopentane at the pressure of saturated vapor. "L" includes the external work done during the increase of volume. I have not access to the original data of Young, but have put in Column 7 of Table II the results as quoted by Dieterici¹ for the internal heat of vaporization, to which I have added the calculated values of the external work, given by $p(v_2 - v_1)$. In calculating L, we have used Equation 32, according to which, $L = 2RT \log_e d_1/d_2 = a_1(1/v_1 - 1/v_2)$. Assuming the values as quoted by Dieterici to be correct, our formula gives too high results, especially at low temperatures. Near 0° C., the error amounts to 10% and becomes as low as 1.7% at 150° C., increasing thereafter as we approach the critical temperature.

I have studied fluorobenzene, normal hexane, carbon tetrachloride with results quite similar to those obtained in the case of isopentane. I shall not take up space discussing them but proceed to a consideration of carbon dioxide.

Carbon Dioxide.—The results in Tables III and IV refer to one gram of carbon dioxide, but the unit of pressure is one atmosphere and the unit of volume one cubic centimeter. According to Amagat,² from whom the data are taken, the critical temperature is 31.35° C. The fifth column of Table IV contains values of the heat of vaporization obtained by Dieterici³ from Amagat's experimental results.

¹ *Ann. Physik*, 9, 176 (1903).

² *Ann. chim. phys.*, [6] 29, 118–136 (1893).

³ *Loc. cit.*

TABLE III.—CARBON DIOXIDE; UNIT MASS = 1 g.

t° C.	v_1 cc.	v_2 cc.	b cc.	a_1 Atm.-cc ²	a_2 Atm.-cc ²	a_3 Atm.-cc ²	a_4 Atm.-cc ²
0	1.094	10.41	0.9900	2806	2731	2758	2414
5	1.126	8.772	0.9980	2751	2680	2712	2443
10	1.168	7.518	1.0109	2719	2636	2671	2412
15	1.229	6.329	1.0292	2673	2595	2632	2404
20	1.306	5.262	1.0463	2647	2549	2586	2400
25	1.422	4.167	1.0602	2581	2493	2522	2408
27	1.490	3.759	1.0670	2557	2472	2498	2408
28	1.532	3.547	1.0699	2543	2461	2484	2407
29	1.587	3.301	1.0717	2523	2449	2468	2409
30	1.672	2.994	1.0729	2494	2436	2449	2414
31	1.866	2.551	1.0777	2465	2427	2432	2420
31.35	2.155	2.155	1.0775	2447	2421	2421	2421

TABLE IV.—CARBON DIOXIDE; UNIT MASS = 1 g.

t° C.	P (obs.) Atm.	$P = \frac{RT}{b} e^{-\frac{a_1}{2bRT}}$	L (calc.) Calories.	L (Dieterici).
0	34.3	31.9	55.7	55.0
5	39.0	36.4	51.6	51.0
10	44.2	40.9	47.7	47.5
15	50.0	46.0	42.7	42.5
20	56.3	51.7	37.0	36.4
25	63.3	58.7	29.0	28.5
27	66.2	61.7	25.1	24.8
28	67.7	63.3	22.9	23.1
29	69.2	65.1	20.0	20.2
30	70.7	67.4	16.0	16.0
31	72.3	70.1	8.6	8.6
31.35	72.9	71.3	0	0

The results in Table III are somewhat similar to those for isopentane. Again a_1 , a_2 and a_3 show general agreement, but the values of a_4 seem to be irregular, in no case diverging very much from the value at the critical temperature. Table IV shows again that the pressures calculated by our formula are usually too low, while on the other hand our calculated values of L agree very well with those of Dieterici.

The experiments of Amagat on the compressibility of carbon dioxide allow us to calculate a and b above the critical temperature. Amagat has given for a series of temperatures up to 258° C. the minimum values of pv as well as the corresponding pressures. His data are reproduced in Table V. Equations 12 and 13, which concern us here, may be written as follows:

$$a = v(a/b - RT) \quad (12)$$

$$\frac{a}{bRT} e^{1 - \frac{a}{bRT}} = \frac{pv}{RT} \quad (13)$$

Using Equation 13 for any temperature and its corresponding value of

pv , the value of a/bRT may be calculated by a rather laborious trial method; thence the value of a/b is obtained, then a from Equation 12 and finally b . A study of Amagat's results and his diagrams will show that although the minimum value of pv may be determined with some accuracy, the value of the corresponding p ; and hence of v , cannot be estimated so precisely. An error in locating the minimum of the curve, especially at high temperatures where the curves are rather flat, will not affect the value of pv very much, but will seriously influence the value of p and v . Hence at the highest temperatures, the values of the pressures as given by Amagat must be allowed to be less accurate than those at lower temperatures. Hence the ratio a/b is probably more accurately determined than a and b .

In Table V the unit mass of carbon dioxide is that which has a volume of 1 cc. at 0° C. when the pressure is one atmosphere. In order to compare the results of Table III with those of Table V, the values of a and b in the former table must be divided by $(505.9)^2$ and 505.9, respectively, since one gram of carbon dioxide occupies 505.9 cc. at 0° C. and one atmosphere. If we select the values of a and b at 20° and 30° in Table III, we shall obtain in the new units: at 20° , $a = 0.009960$, $b = 0.002068$; at 30° , $a = 0.009518$, $b = 0.002121$. These values agree very well indeed with those in Table V obtained in quite a different way.

TABLE V.—CARBON DIOXIDE: $v = 1$ AT 0° C. WHEN $p = 1$ ATMOSPHERE.

t° C.	p , Atm.	p , Minimum.	$v \times 10^3$, cc.	a/bRT .	a/b .	$a \times 10^3$, Atm.-cc.	$b \times 10^3$, cc.
20	56.8	0.1475	2597	4.497	4.868	9829	2019
30	76	0.2185	2875	4.027	4.508	9741	2161
40	101	0.3083	3053	3.604	4.168	9192	2206
50	125	0.3965	3172	3.294	3.931	8683	2209
60	143	0.4830	3378	3.050	3.752	8519	2270
70	162	0.5690	3512	2.847	3.608	8218	2278
80	179	0.6500	3631	2.683	3.500	7972	2278
90	196	0.7310	3730	2.538	3.404	7694	2260
100	210	0.8140	3876	2.403	3.312	7495	2263
137	245	1.0850	4429	2.053	3.109	7078	2271
198	255	1.4920	5851	1.661	2.891	6733	2329
258	218	1.8100	8303	1.456	2.857	7433	2602

The results shown in Table V indicate that a continues to decrease above the critical temperature, while b , if it increases at all, increases very slowly. The values for a and b at 258° and probably also at 198° are likely subject to a considerable error, as has already been pointed out. Our results justify us therefore in saying that above the critical temperature and up to 200° C. b remains essentially constant in the case of carbon dioxide.

I may state here that results quite similar to those for carbon dioxide are obtained with ethylene, when Equations 12, 13 and 14 are applied

to Amagat's results. In the case of ethylene also, b seems to remain fairly constant from 10° to 198° , while a decreases as the temperature rises.

An application of the set of Equations 17 may be made to carbon dioxide. According to these equations, at the critical temperature, the value of the minimum pv is $\frac{2}{e} p_c v_c$, the corresponding pressure is $1.104 p_c$

and the volume is $\frac{2}{3} v_c$ or $\frac{4}{3} b_c$. Now interpolating in Table V between 30° and 40° , we find for 31.35° , $p = 79.4$, $pv = 0.2302$, $v = 0.002899$, while in the same units, $p_c = 72.9$, $v_c = 0.004260$. $b_c = 0.002130$. The calculated values for minimum pv would be: $p = 80.4$, $pv = 0.2286$. $v = 0.002840$, agreeing very well with the interpolated values.

Hydrogen.—In discussing hydrogen, we shall take as unit mass that quantity of hydrogen which occupies one cubic centimeter at 0° C. and the pressure of one atmosphere. According to Witkowski,¹ the behavior of this gas at 0° C. is given accurately by the equation

$$pv = 0.999384 + \frac{0.0006154}{v} + \frac{0.000000706}{v^2}.$$

The Dieterici equation at low pressures may be written

$$pv = RT + bp - a/v^2.$$

If we imagine the pressure to be reduced indefinitely and the volume correspondingly increased, we find by comparing this equation with that of Witkowski that at 0° C. $RT = 0.999384$ and hence $R = 0.0036595$. To avoid any misconception, it might be explained that the reason this value of R differs from $1/273.09 = 0.0036618$, is because our unit mass of hydrogen which occupies one cubic centimeter under standard conditions, would occupy only 0.999384 cc. if it were a "perfect" gas. Hence the value of R is smaller to that degree.

The critical temperature and pressure of hydrogen have been determined by a number of investigators. Bulle² has recently obtained the following values: $T_c = 31.95 \pm 0.1^\circ$ and $p_c = 11.0$ atmospheres. Since $T_c = a/4Rb$ and $p_c = a/4e^2b^2$, we obtain from Bulle's data, $a/b = 0.4677$, $a = 0.000673$, and $b = 0.001439$. The minimum values of pv have been determined by Witkowski³ and by Kamerlingh Onnes and Braak.⁴ The earlier results of Witkowski agree fairly well with those of Onnes and Braak, although Witkowski states that his determinations of the pressures corresponding to a minimum pv may be several atmospheres in error. The results obtained by applying Equations 12, 13

¹ *Bull. acad. Cracovie*, 6, 305-338 (1905).

² *Physik. Z.*, 14, 860-2; *C. A.*, 7, 3877 (1913).

³ *Loc. cit.*

⁴ *Comm. Phys. Lab., Leiden*, No. 97 (1907); quoted in Young's "Stoichiometry," p. 24.

and 14 to the data of Witkowski and of Onnes and Braak are set forth in Tables VI and VII, respectively. Both tables would indicate that the ratio a/b is approximately constant in the temperature interval under investigation. The results from Witkowski's data seem to show a decrease of both a and b with rise of temperature, while the presumably more accurate data of Onnes and Braak exhibit a and b as essentially constant from -217° C. to -183° C. The values of a and b in Tables VI and VII should be compared with those I have calculated from the critical data. In both tables the values of a are considerably smaller than that of a at the critical temperature; but whereas Witkowski's data indicate smaller values of b , those of Onnes and Braak give us values

TABLE VI.—HYDROGEN DATA OF WITKOWSKI. $v = 1$ AT 0° C. WHEN $p = 1$ ATM.

t° C.	p . Atm.	pv . Min.	a/bRT .	a/b .	$a \times 10^4$. Atm.-cc ² .	$b \times 10^4$. cc.
-183	32	0.3270	1.1334	0.3737	449	1203
-190	43.5	0.2970	1.2329	0.3749	484	1290
-205	55	0.2273	1.4920	0.3718	507	1363
-212	54.8	0.1926	1.6496	0.3688	511	1384

TABLE VII.—HYDROGEN DATA OF ONNES AND BRAAK. $v = 1$ AT 0° C. WHEN $p = 1$ ATM.

t° C.	p . Atm.	pv . Min.	a/bRT .	a/b .	$a \times 10^4$. Atm.-cc ² .	$b \times 10^4$. cc.
-182.75	33.36	0.32630	1.1707	0.3870	552	1426
-195.20	47.69	0.27338	1.3175	0.3756	519	1382
-204.62	52.10	0.22935	1.4816	0.3712	531	1431
-209.6	53.73	0.20394	1.6011	0.3720	530	1425
-212.73	53.63	0.18780	1.6827	0.3717	528	1421
-217.32	51.57	0.16335	1.8234	0.3721	532	1430

TABLE VIII.—HYDROGEN. DATA OF WITKOWSKI.

p (Atm.) Witkowski.	$t = -183^{\circ}$ C. p (calc.).	$t = -190^{\circ}$ C. p (calc.).	$t = -205^{\circ}$ C. p (calc.).	$t = -212^{\circ}$ C. p (calc.).
1	1.004	1.005	1.006	1.009
5	5.008	5.010	5.014	5.026
10	9.997	9.995	10.003	10.016
15	14.995	14.990	14.986	15.013
20	20.013	20.007	19.989	20.089
25	25.011	24.999	25.023	25.065
30	30.002	30.005	30.058	30.088
35	35.003	35.000	35.093	35.139
40	40.024	40.007	40.079	40.167
45	45.028	45.003	45.036	45.126
50	50.020	49.997	50.005	50.026
55	54.997	54.977	55.000	54.998
60	59.955	59.958	60.007	60.052

not appreciably different from the value of b at 32° absolute. We shall, however, shortly produce evidence indicating that, above -183° C. at least, a and b for hydrogen do decrease with rise of temperature. Before proceeding to this, I desire to illustrate how well the Dieterici equa-

tion reproduces the Witkowski data. Witkowski¹ gives a table containing the values of pv at a series of temperatures from 100°C. to -212°C. and up to a pressure of 60 atmospheres. In Table VIII I have given the results of calculating the pressures corresponding to volumes as given by Witkowski and at the temperatures -183° , -190° , -205° , and -212°C.

I have used the equation $p = \frac{RT}{v-b} e^{-\frac{a}{vRT}}$, where R is equal to 0.0036595, and the values of a and b for each temperature are taken from Table VI. The agreement of the calculated pressures with those given by Witkowski is certainly very excellent. It is to be noted that the values of a and b which have been employed have not been deduced from the whole course of the pv curve, but in each case from its minimum value only.

According to Equation 7a, we have the relation

$$\left(\frac{dp}{dT}\right)_v = \frac{p}{T} \left(1 + \frac{a}{vRT} + \frac{T}{v-b} \cdot \frac{db}{dT} - \frac{1}{vR} \frac{da}{dT}\right) = \frac{R}{v-b} e^{-\frac{a}{vRT}} \left(1 + \frac{a}{vRT} + \frac{T}{v-b} \frac{db}{dT} - \frac{1}{vR} \frac{da}{dT}\right) \quad (7a)$$

If a and b are constants, or if the expression $(T/(v-b) \cdot db/dT - 1/vR da/dT)$ vanishes, we have the simpler equations

$$\left(\frac{dp}{dT}\right)_v = \frac{p}{T} \left(1 + \frac{a}{vRT}\right) = \frac{R}{v-b} e^{-\frac{a}{vRT}} \left(1 + \frac{a}{vRT}\right). \quad (7)$$

In most cases, where v is not too small, we could write

$$\left(\frac{dp}{dT}\right)_v = \frac{R}{v-b}. \quad (7b)$$

I have assumed that the expression $\frac{T}{v-b} \frac{db}{dT} - \frac{1}{vR} \frac{da}{dT}$, in what follows, is very small, compared with a/vRT in the case of hydrogen, at least throughout the temperature interval -183°C. to 100°C. The grounds for this will be discussed later. I have accordingly used Equation 7 to determine a and b , calculating $(dp/dT)_v$ and P/T from the Witkowski data. In his memoir, Witkowski gives the pressures at the series of temperatures, 100° , 0° , -77° , -104° , -147° , -183° , -190° , -205° , and -212°C. , corresponding to a series of volumes from 1 to $1/60$ in terms of the volume at 0°C. and one atmosphere. The method I employed to obtain an accurate estimate of $(dp/dT)_v$ at each temperature will be clear from the following example: Corresponding to the volume $v = 1/40$, Witkowski gives for the temperatures -77° , -104° , and -147°C. the pressures 29.33, 25.22 and 18.63, respectively. An equation of the second degree in T was found algebraically which would re-

¹ *Loc. cit.*

produce the pressures at the three temperatures. From this equation, the values of (dp/dT) , at -104° was easily calculated. Geometrically, having pressures as ordinates and temperatures as abscissae, a parabola was found which would go through the three points and the slope at the intermediate point was the value sought. The parabola, of course, in no case departs much from a straight line. To find (dp/dT) , at -147° C., the data for -104° , -147° and -183° were used and so on for all the other temperatures. It is evident that the values we have obtained for (dp/dT) , will, in all probability, be more accurate at higher temperatures than at lower ones. The pressures at 0° C. are more than four times as great as at -205° C., and as (dp/dT) , is obtained by a different method, the probable error at -205° will be four times as great as at 0° C., assuming that the pressures in both cases have been determined with the same relative accuracy. I have determined (dp/dT) , and hence a and b , using the data for the volumes $1/60$, $1/50$, $1/40$, $1/30$ and $1/20$ for the temperatures already named, excluding the highest and the lowest one. Here again the accuracy of the calculated result will, for obvious reasons, be inversely proportional to the volume selected. This will be illustrated by the results obtained at the various volumes, although there is a surprising agreement in nearly all cases.

In Table IX are given the detailed results for $v = 1/60$, while Table X contains only the final results for a , b , and a/b , with the averages in the last column, excluding from the average the results for $v = 1/20$, which are likely to be least accurate. Table XI is simply a summary of these average values together with the values for 100° C., obtained by a rather uncertain extrapolation. As emphasized previously, the results at low temperatures are probably less trustworthy than those at higher temperatures. An examination of these tables shows that a and b decrease with rise of temperature. With regard to the ratio a/b , the same statement may actually be true, in spite of the fact that from -205° to -147° the tables indicate a slight increase with the temperature. The results at low temperatures are, however, subject to such error that it is unsafe to indulge in much generalizing. An important point to be noted, however, is that the values of a , b , and also a/b , as found by the present method for -183° , -190° and -205° C., agree remarkably well with those given in Tables VI and VII, found by a quite different method. The equation of state for a gas at low pressures can be written in the form $pv = RT + p(b - a/RT)$, which at 0° C. is equivalent to $pv = RT + p(b - a)$, since RT is approximately unity. Comparing this with Witkowski's empirical equation already given, we find the value of $(b - a)$ at 0° C. to be 0.0006154 . From Table XI we obtain a result in very satisfactory agreement with this value, viz., $(b - a) = 0.000622$.

TABLE IX.—HYDROGEN. $v = 1$ AT 0° C. WHEN $p = 1$ ATM.
 $v = 1/60$.

t° C.	p . Atm.	p/T .	$\left(\frac{dp}{dT}\right)_{v=1/60}$.	a/vRT .	$a \times 10^4$. Atm.-cc.	$b \times 10^4$. cc.	a/b .
100	(85.422)
0	62.331	0.22824	0.23136	0.01367	228	851	0.2679
-77	44.49	0.22688	0.23229	0.02385	285	910	0.3132
-104	38.21	0.22597	0.23337	0.03231	333	993	0.3353
-147	28.10	0.22286	0.23505	0.05471	421	1120	0.3759
-183	19.64	0.21800	0.23679	0.08619	473	1273	0.3716
-190	17.98	0.21639	0.23720	0.09668	490	1306	0.3752
-205	14.42	0.21178	0.24110?	0.13844	575	1621	0.3547
-212	12.72

TABLE X.—HYDROGEN. a AND b MULTIPLIED BY 10^4 .

		$v = 1/60$.	$v = 1/50$.	$v = 1/40$.	$v = 1/30$.	$v = 1/20$.	Mean, excluding those for $v = 1/20$.
0°	a	228	226	232	213	249	225
	b	851	849	854	834	864	847
	a/b	0.2679	0.2662	0.2718	0.2558	0.2878	0.2652
-77°	a	285	302	299	314	375	300
	b	910	942	939	963	1026	938
	a/b	0.3132	0.3202	0.3188	0.3261	0.3655	0.3197
-104°	a	333	360	360	366	396	355
	b	993	1027	1028	1032	1049	1020
	a/b	0.3353	0.3501	0.3500	0.3544	0.3775	0.3480
-147°	a	421	406	421	430	415	419
	b	1120	1089	1120	1144	1110	1118
	a/b	0.3750	0.3729	0.3761	0.3756	0.3739	0.3748
-183°	a	473	486	478	487	604	481
	b	1273	1313	1277	1312	1613	1294
	a/b	0.3716	0.3701	0.3746	0.3710	0.3745	0.3717
-190°	a	490	506	510	531	652	509
	b	1306	1372	1383	1448	1770	1377
	a/b	0.3752	0.3689	0.3685	0.3667	0.3684	0.3696
-205°	a	575	544	567	625	731	578
	b	1621	1506	1572	1760	2045	1615
	a/b	0.3547	0.3615	0.3609	0.3551	0.3575	0.3579

TABLE XI.—HYDROGEN. AVERAGE VALUES OF a , b AND a/b FROM TABLE X.

	0° .	-77° .	-104° .	-147° .	-183° .	-190° .	-205° .	$+100^{\circ}$ C. (extrapolated).
$a \times 10^4$	225	300	355	419	481	509	578	170?
$b \times 10^4$	847	938	1020	1118	1294	1377	1615	800?
a/b	0.2652	0.3197	0.3480	0.3748	0.3717	0.3696	0.3579	0.2125?

For an ideal gas, we have the relation $p/T = R/v$. For the mass of hydrogen which we are taking as our unit and for a value of v equal to $1/60$, the theoretical value of p/T would be 0.21957. An examination of the third column of Table IX will show that somewhere between -147°

and -183° , p/T has its "theoretical" value. By interpolation, we find this temperature to be -171.4° . If we investigate the data for $v = 1/50$, $1/40$, $1/30$ and $1/20$, we obtain the following results for this temperature, viz., -171.4° , -170.3° , -157.5° , -167.0° . Since the results for $v = 1/60$ and $1/50$ are the most accurate, we may accept -171.4° C. as very close to the temperature at which $p/T = R/v$. Now, according to the equation of state, for moderate pressures,

$$\frac{p}{T} = \frac{R}{v-b} e^{-\frac{a}{vRT}} = \frac{R}{v} \left(1 + \frac{b}{v} - \frac{a}{vRT} \right).$$

Evidently p/T will equal R/v when $b = a/RT$, or $a/b = RT$. Since we have found the temperature to be -171.4° , we calculate for this temperature $a/b = RT = 0.3721$, in excellent agreement with the values of a/b in Table XI. At the temperature -171.4° C. or 101.6° absolute, the pv curve for hydrogen would just fail to have a minimum and would proceed virtually horizontally for several atmospheres. At this temperature, the behavior of hydrogen under moderate pressures would be given very accurately by Boyle's law.

Joule-Thomson Effect for Hydrogen.—The values we have obtained for a and b , at least at 0° and 100° C., are confirmed if we consider their relation to the Joule-Thomson effect. According to the experiments of Joule,¹ the value of $\Delta T/\Delta p$ of Equation 34, at 6.8° C. is -0.030 , and at 90.1° C. is -0.044 . We can use at 6.8° C. the values of a and b for 0° C. Their values near 100° C. will be less and a rough extrapolation gives us for 100° C., $a = 0.000170$, and $b = 0.000800$. Using our values of a and b in Equation 34, the calculated value of $\Delta T/\Delta p$ at 6.8° C. would be -0.032 , and at 90.1° C. -0.043 , in good agreement with the observed values. The negative lowering means, of course, an elevation of temperature.

Whether there shall be a rise or a fall in temperature in the Joule-Thomson experiment depends on whether $(2a/RT - b)$ is negative or positive. For most gases at ordinary temperatures b is less than $2a/RT$ and we have a fall in temperature. In the case of hydrogen at ordinary temperatures $(2a/RT - b)$ is negative and we have a rise in temperature. At a sufficiently low temperature the sign should be reversed. The inversion temperature for hydrogen has been found by Olszewski² to be -80.5° C. or 192.5° abs. At this temperature, then, we should have $(2a/RT - b) = 0$. Now using the values given in Table XI, at -77° C., $(2a/RT - b) = -0.000102$ and at -104° C. $(2a/RT - b) = +0.000128$. Accordingly, at about -89° C. or 184° abs. $(2a/RT - b)$ would be zero. We therefore calculate the inversion temperature to be 184° instead of 192.5°

¹ Landolt-Börnstein's *Tabellen*, 1912, p. 786.

² *Bull. acad. Cracovie*, 1901, p. 453; quoted in Young's "Stoichiometry," p. 236.

abs. as observed by Olszewski. This investigator later observed in the case of nitrogen and oxygen that the inversion temperature depends on the initial pressure. Equation 34 in its most rigorous form would also show that this must be the case. In any event, the fair agreement of our value with that observed by Olszewski is another confirmation of the approximate correctness of the values we have obtained for a and b .

We are now in a better position to consider the assumption we have made that in the equation

$$\left[\frac{dp}{dT} \right]_v = \frac{p}{T} \left[1 + \frac{a}{vRT} + \frac{T}{v-b} \frac{db}{dT} - \frac{1}{vR} \frac{da}{dT} \right]$$

we may suppose $\frac{T}{v-b} \frac{db}{dT} - \frac{1}{vR} \frac{da}{dT}$ to be negligible with respect

to a/vRT . All our values from -205° to 0° C. have been calculated on this assumption, in applying Equation 7. The assumption seems to have been justified by the following facts: (1) The values we have obtained at -183° and -190° (cf. Table XI) agree well with those calculated from the minimum values of pv (cf. Tables VI and VII). (2) When the values of a and b from Table XI are used in the equation $p =$

$\frac{RT}{v-b} e^{-\frac{a}{vRT}}$, the experimental results of Witkowski are reproduced

with great accuracy (cf. Table VIII). (3) At 0° C., our values of a and b agree well with the value of $(b - a/RT)$ or $(b - a)$ deduced from Witkowski's empirical equation. (4) Our values of a and b at 0° C. and 100° C. lead us to an estimate of the Joule-Thomson effect in good agreement with experiment. (5) Our calculation of the inversion temperature agrees passably well with Olszewski's observation. (6) At 0° C. the value of $(b - a/RT)$, or in this case $(b - a)$, is determined with some degree of precision by Witkowski's work to be close to 0.000620. All our experience with isopentane, carbon dioxide and other substances not considered in this paper goes to show that a always decreases with rise of temperature. Since at the critical temperature and around -183° C., $(b - a)$ is much greater than 0.000620, the value of b must decrease with rise of temperature to 0° C. Since a and b decrease together, the terms $\frac{T}{v-b} \frac{db}{dT}$ and $-\frac{1}{vR} \frac{da}{dT}$ will tend to neutralize each other; and the

preceding statements go to show that this neutralization is fairly complete.

These considerations seem to justify the assumption I have made and to render the values of a and b which I have obtained worthy of some degree of confidence. That b decreases with rise of temperature, at least above -183° C., is a result in harmony with the views expressed by T. W. Richards¹ in regard to the compressibility of atoms. He shows that

¹ THIS JOURNAL, 36, 617 (1914); 37, 2417 (1915).

the value of b for helium (assuming that a is negligible) decreases from 0°C. to 100°C. , and explains the decrease as due to the increasing collision-pressure with increase of temperature. Whatever be the explanation, we have found that the same thing is true of b for hydrogen, its value at 0°C. being about 60% of that at the critical temperature.

Our calculations for helium are also in harmony with those of T. W. Richards. According to Kamerlingh Onnes,¹ the critical temperature for helium is 5.25° abs. and the critical pressure 1718 millimeters, or 2.261 atmospheres. From these data we obtain $a = 0.000089$ and $b = 0.001151$, where the unit quantity of helium occupies one cubic centimeter under standard conditions. Evidently the value of a is very small and at ordinary temperatures one is probably justified in considering a/RT negligible with reference to b . If we take 4 g. of helium as our unit mass, the value of b at 5.25° abs. is 25.6 cc. At 0°C. and at 100°C. Richards finds $(b - a/RT)$ or in this case, very approximately, b , equal to 12 cc. and 10.4 cc., respectively. The value of b at 0°C. is thus less than half what it is calculated to be at $5.25^\circ \text{ absolute.}$

In the case of hydrogen, however, the value of a/RT is not negligible with respect to b and for this reason fairly accurate values of both must be determined before one can say whether b decreases or not with the temperature. Thus Richards finds an increase in $(b - a/RT)$ for hydrogen as one goes from 0°C. to 100°C. In spite of this fact, we have found that both a and b decrease in this interval. Richards, of course, fully understood that this might be the case, if the value of a were sufficiently large.

Richards has also expressed the view that b does not differ very much from the volume of the liquefied gas. Our results are so far in agreement with this, that we have found b at temperatures considerably below the critical temperature to be but slightly smaller than the volume of the liquid, as is apparent from the equation $1/b = 1/v_1 + 1/v_2$.

So far we have not particularly concerned ourselves with the question as to whether a and b in addition to being temperature, are also volume functions. The critical state is determined mathematically by the condition that $(dp/dv)_T$ and $(d^2p/dv^2)_T$ shall both be zero. Assuming a and b to be independent of the volume has led to results in conformity with experience; for example, to the result that the critical density is 3.695 times as great as the density would be for an "ideal" gas at the critical temperature and pressure. I have therefore felt myself justified in inferring that a and b are essentially independent of the volume within the limits of pressure considered in this paper. It is only right to state, however, that when very great pressures are considered, it seems

¹ C. A., 7, 2327 (1913).

necessary, as a result of some calculations I have made, to assume that b under these circumstances suffers a diminution in volume. This question I have, however, not investigated thoroughly, partly owing to the lack of available, accurate data.

As a result of the investigation set forth in this paper, I consider that the following statements are justified: The Dieterici equation of state has a sounder theoretical basis than that of van der Waals. It reproduces the behavior of a gas, not only at low pressures, but also at the critical point and even at much higher pressures. Although, perhaps, not so simple an expression as van der Waals's, many of the deductions from it are characterized by great simplicity and elegance. It has of course the great advantage over the van der Waals equation that it reproduces the critical state accurately, whereas the latter, as is well known, does not. It seems to me, therefore, that we ought to abandon the van der Waals equation, except as a qualitative interpretation of the facts, and adopt the Dieterici equation of state as the only one which has both a sufficiently sound theoretical foundation and a sufficiently accurate correspondence with the facts.

Summary.

In the present paper I have discussed the Dieterici equation of state,
$$p = \frac{RT}{v-b} e^{-\frac{a}{vRT}}$$
 in some detail and have indicated in a number of ways how accurately it reproduces the experimental results.

Various methods are developed for calculating the values of a and b below, at, and above the critical temperature.

A formula is deduced for calculating the pressure of saturated vapor from the densities of the liquid and vapor.

A formula is deduced for calculating the latent heat of vaporization from the densities of liquid and saturated vapor.

Isopentane, carbon dioxide and hydrogen are studied in some detail. In the case of isopentane, a decreases and b increases from 0°C. up to the critical temperature. The same is true of carbon dioxide. Above the critical temperature, in the case of carbon dioxide, a continues to decrease, while b remains fairly constant up to 200°C. In the case of hydrogen, a decreases from the critical temperature up to ordinary temperatures, while b does the same, from -183°C. at least.

In the case of hydrogen, its inversion temperature is calculated, and also the temperature at which it "obeys" Boyle's law for moderate pressures. The latter temperature was calculated to be -171.4°C.

Combining the law of Cailletet and Mathias with a result obtained by Young for a number of substances, it is shown that the density of a substance at the absolute zero is four times the critical density.

Our conclusions in regard to the variation of b with the temperature

are shown to be in harmony with some of the views of T. W. Richards in regard to the compressibility of atoms.

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THE PROPERTIES OF MIXED LIQUIDS. I. SULFURIC ACID-WATER MIXTURES.

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This paper is the first report upon a somewhat extended series of investigations, started some two years ago, upon the drop weights, or surface tensions, of pure liquids, at many temperatures, and their relationship to the values of that property in their binary or other admixtures in various proportions, at those temperatures. The main object of the work is to provide such a further, perhaps more consistent, set of experimental data that eventually it may perhaps be possible to find the cause of the mutual effects of liquids upon one another; which, although absent in some cases, are great, and yet of widely differing magnitude, in others.

For some binary liquid mixtures it is known that the so-called *law of mixtures* holds more or less rigidly, *i. e.*, the value of a certain physical property of the mixture is equal to the sum of the values of that property for the pure constituents under like conditions, each multiplied by the ratio of its weight in the mixture, to the total weight of the system. Or, expressed as an equation, $P_{\text{Mixture}} = xP_a + (1-x)P_b$, where the terms P represent the values of the property considered, and x is the weight of the constituent a , when the total weight of the mixture is regarded as unity. In all cases of this sort it is generally assumed, apparently with reason, (1) that no chemical reaction has taken place between the constituents, and (2) that the previous molecular state of each constituent in the pure condition still persists in their mixture.

The great mass of binary liquid mixtures, however, not only fails to follow this law, but shows a variation from it which depends solely upon the constituents selected, and upon the proportions in which they are mixed. From the fact that following the law of mixtures is regarded as indicating that a system is free from any chemical interaction between its constituents, and that the molecular states of its constituents are unaltered as a result of the mixing, it is natural to assume that a system which does not follow this law is one in which either a chemical reaction has taken place, or in which the constituents have undergone a molecular change, of the nature of a breaking down of a previous polymerization of one or both of the individuals, for example.

Many investigators, ignoring the second possible cause of change,

have assumed that, from the curve obtained by plotting the results of some one of the various physical properties of a system, which does not follow the mixture law, against the percentage composition of the mixture, it is possible not only to conclude that a chemical compound has been formed, but actually to calculate its formula. Washburn,¹ however, after an exhaustive review of the previous work, has concluded that in all such property-composition curves "supposed points of discontinuity are due to experimental error".....although "striking irregularities sometimes occur." Next, quoting the fact brought out by Tammann that "as regards certain of its physical properties a salt solution resembles the pure solvent under an increased external pressure"....he shows how this might "cause a dissociation of complex molecules into simple ones".....the effect of which would be that "a large part of the abnormal effects of salts upon the physical properties should also be ascribed to changes in the complexity of the solvent." Washburn's final conclusion, which may be regarded as the last word upon the subject of the physical properties of mixed liquids as it was then understood, is that "methods of studying hydration which depend upon the deviation of any physical property of a solution from the law of mixtures are incapable of yielding any *conclusive* information regarding the complexity or even the existence of hydrates in aqueous solution."

The later work of Denison,² however, has modified the above conclusion decidedly, at least in so far as it concerns mixtures of liquids, and apparently not only enables us to differentiate between the effects due to a change in the molecular states of the individual constituents, and those due to their chemical interaction, but also actually does make possible the calculation of the formula of the chemical compound formed in the latter case. Denison's method of attack was theoretical, in that he assumed in a hypothetical system that the various possible changes had taken place to different extents, and studied the curves thus obtained. In this manner he showed first, confirming Washburn's statement, that "a maximum or minimum in the property-composition curve must be taken as giving *possible* indication of the formation of a chemical compound, although there is no certainty." At the same time he calls attention to the fact that a sagged curve (without maxima or minima) may be caused by either a dissociation of one of the constituents, or by their chemical combination, but that a process involving increased association of one of the constituents as a result of their mixing is unlikely.

It is not the property-composition curve, however, but that for which the coördinates are composition and *deviation* from the mixture law, that leads to indications of chemical interaction between the constituents

¹ *Tech. Quart.*, 21, 360 (1908).

² *Trans. Faraday Soc.*, 8, 20, 35 (1912).

of mixed liquids. Denison's conclusions from curves of this form may be summarized briefly as follows:

The magnitude of the deviation from the mixture law is proportional to the amount of new substance formed, and always reaches a maximum when the concentration of the new substance attains a maximum value; and further, when this is true, the mixture as a whole has the same fractional composition as the new substance formed. Although temperature changes may affect the form of the property-composition curve, especially as regards the maximum point, the point of maximum *deviation* from the mixture law is independent of temperature change.

If the above be true, and aside from any consideration of the merits of the theoretical reasoning involved, the few applications of it by Denison himself are convincing, it will be seen that it is possible to determine the formula of a compound formed by the interaction of the constituents of a mixed-liquid system by aid of the physical properties alone, since the composition of the compound formed must invariably be identical with the composition of that mixture which exhibits the maximum deviation from the value calculated by aid of the mixture law. In other words, if Denison's conclusion be true, we can get as definite information from it for homogeneous liquid systems, as we can by the application of the phase rule to non-homogeneous systems.

In the course of the present series of investigations it is intended, among other things, to apply this proposed method of plotting results, not only with respect to surface tension, but also to all other physical properties that can be readily measured at the time, or for which results are given in the literature; in other words, to subject the method to a thorough experimental test.

The Determination of the Surface Tension.

The surface tensions of the sulfuric acid-water mixtures were determined by the drop-weight method,¹ the dropping tip, which in all cases gave drops for these solutions that were "normal" in profile, being standardized by aid of water at three temperatures, with the following result, each drop-weight value being the mean of several measurements, agreeing to within a few hundredths of one per cent.

t.	w _{H₂O} (mgs.).	γ _{H₂O} (dynes).	Constant = $\frac{\gamma_{H_2SO_4}}{\gamma_{H_2O}}$
0	80.93	75.75 ²	0.9360
30	75.88	71.03	0.9361
50	72.21	67.59	0.9360
Average,			0.9360

¹ See Morgan, *THIS JOURNAL*, 37, 1461 (1915).

² This value is for water unsaturated with air. If air is bubbled through the liquid just before the determination, the values of both γ and w are slightly larger at 0°, viz., γ = 75.87; but since this process is impossible in the later work with solutions, owing

The surface tension of a liquid can thus be found in dynes per centimeter at any temperature, from its drop weight in milligrams from this tip at that temperature, by aid of the equation

$$\gamma_{l,t} = 0.9360 \times w_{l,t}.$$

The value of this constant was redetermined frequently during the course of the work and found to remain unchanged. From the value of this constant the mean diameter of the tip used is calculated to be approximately 5.35 millimeters.¹

Owing to the very viscous nature of sulfuric acid solutions from 60 to 90% content, and their consequent lack of what might be called covering power, difficulty was at first experienced in driving the drop out to the extreme edge of the tip. This trouble can be readily avoided in the case of all viscous liquids, however, by forcing the first drop out rapidly and nearly to maturity, and then quickly withdrawing it. This process is to be repeated perhaps a dozen times, until the tip is seen to be completely covered, after which each new drop, formed in the usual way, goes out of itself to the same extent, *i. e.*, to the extreme edge of the tip, just as non-viscous liquids do without aid.

As in all previous work with solutions, the weighing vessel is first charged with a small amount of the liquid, the vessel and contents being weighed before it is attached to the apparatus and placed in the thermostat. When the proper temperature is attained, the desired number of drops are allowed to form and fall, and the vessel removed and again weighed with its contents. The difference in the two weighings thus gives the weight of the fallen drops. In this way, the concentration of the first and succeeding drops remains unchanged, for evaporation is prevented by the vapor already present from the inclosed liquid.

The thermometer used in the work was a certified one, the temperatures being fixed to within $\pm 0.05^\circ$, while the weights employed had been compared with a standard set.

The sulfuric acid which served as a basis for the solutions was a good "C. P." acid of specific gravity 1.84. Both gravimetric and volumetric analyses of this sample showed that it contained 96.12% of H_2SO_4 , and therefore, 3.88% of water, by weight. Solutions up to 96.12% acid were made from this by the addition of calculated amounts of distilled water, while those of higher concentration were prepared by adding various amounts of pure sulfur trioxide. The 100% acid thus produced had a melting point of 10.40° . All the solutions, in addition, were analyzed gravimetrically, with the result that no appreciable differences were found to exist.

to the loss of vapor and consequent change in concentration, the above procedure is to be preferred here. At higher temperatures, the effect of contained air is negligible.

¹ See Morgan, *loc. cit.*, p. 1466.

The results for surface tension, as well as for specific cohesion, of the various solutions studied at three temperatures, are given in the following table. As the actual drop weights observed can be found, of course, from the surface tension results given, by division by the factor 0.9360, to save space, these are omitted in the table. All concentrations are expressed in weights of acid per 100 g. of solution.

TABLE I.—RESULTS.

Column 1, grams H_2SO_4 per 100 g. of solution; 2, mols of SO_3 per 100 mols of mixture; 3, temperature; 4, surface tension in dynes from $\gamma_t = \text{constant} \times w_t$; 5, specific cohesion, a^2 , from γ and d ; 6, specific cohesion from interpolation formulas; 7 and 8, the values of the coefficients α and β of the interpolation formula for the variation in surface tension with temperature, for the concentration in question, viz., $\gamma_t = \gamma_0 + \alpha t + \beta t^2$, where γ_0 in very case is the value presented for that concentration at 0° in Column 4.

1.	2.	3.	4.	5.	6.	7.	8.
0	0	0°	75.75	15.46	15.44		
		30	71.03	14.56	14.46	-0.1485	-0.000294
		50	67.59	13.96	13.90		
4.67 ¹	0.89	0	75.35	14.87	14.91		
		30	71.15	14.15	14.14	-0.1283	-0.00039
		50	67.96	13.64	13.63		
8.93	1.74	0	75.27	14.42	14.40		
		30	71.31	13.80	13.83	-0.1197	-0.00041
		50	68.26	13.34	13.37		
16.40	3.36	0	75.66	13.76	13.79		
		30	71.87	13.25	13.24	-0.1154	-0.000378
		50	68.95	12.84	12.88		
22.73	4.88	0	76.07	13.24	13.23		
		30	72.62	12.84	12.84	-0.0994	-0.00052
		50	69.80	12.48	12.49		
28.18	6.30	0	76.56	12.83	12.84		
		30	73.10	12.46	12.46	-0.1071	-0.000274
		50	70.52	12.16	12.15		
32.90	7.63	0	76.91	12.49	12.48		
		30	73.60	12.16	12.16	-0.1057	-0.000154
		50	71.24	11.91	11.90		
37.05	8.89	0	77.02	12.16	12.16		
		30	73.97	11.89	11.89	-0.0946	-0.000237
		50	71.70	11.66	11.66		

¹ This concentration corresponds within less than 0.1% to that solution investigated in 1912 by Morgan and Bole (THIS JOURNAL, 35, 1756), who used a larger tip, standardized with both water and benzene. An idea of the reproducibility of the surface tension results by the drop-weight method can perhaps be best obtained from the comparison of the two sets of values given below:

1.	M. & B.	M. & D.
0°	75.39	75.35
15	73.33	73.34 (interpolated)
30	71.15	71.15

TABLE I (continued).

1.	2.	3.	4.	5.	6.	7.	8.
40.71	10.07	0	77.05	11.88	11.88		
		30	74.27	11.65	11.65	-0.0838	-0.000297
		50	72.12	11.44	11.44		
		70	69.50		
42.38	10.63	0	77.11	11.75	11.74		
		30	74.34	11.53	11.53	-0.0880	-0.000145
		50	72.35	11.34	11.33		
43.97	11.18	0	77.02	11.61	11.61		
		30	74.39	11.41	11.41	-0.0800	-0.000257
		50	72.38	11.23	11.23		
45.46	11.72	0	76.97	11.49	11.48		
		30	74.42	11.30	11.30	-0.0766	-0.00028
		50	72.44	11.12	11.13		
46.88	12.24	0	76.80	11.36	11.36		
		30	74.46	11.19	11.19	-0.0663	-0.00039
		50	72.51	11.02	11.03		
48.06	12.68	30	74.37	11.09	11.10		
48.23	12.75	0	76.57	11.21	11.24		
		30	74.34	11.07	11.09	-0.0637	-0.00036
		50	72.50	10.92	10.93		
49.51	13.24	0	76.41	11.09	11.12		
		30	74.30	10.97	10.98	-0.0582	-0.00041
		50	72.49	10.82	10.84		
54.10	15.11	0	75.82	10.65	10.67		
		30	74.06	10.59	10.59
		50	72.41	10.46	10.48		
57.86	16.76	0	75.17	10.28	10.29		
		30	73.80	10.27	10.25	-0.0263	-0.00065
		50	72.24	10.16	10.16		
61.08	18.28	0	74.45	9.95	9.92		
		30	73.29	9.96	9.97	-0.0235	-0.00051
		50	72.01	9.90	9.90		
66.23	20.94	0	73.39	9.45	9.45		
		30	72.47	9.49	9.52	-0.0152	-0.00052
		50	71.34	9.45	9.45		
70.18	23.18	0	72.21	9.03	9.06		
		30	71.63	9.12	9.14	-0.0058	-0.00084
		50	70.41	9.06	9.06		
72.95	24.89	0	71.49	8.77	8.75		
		30	71.00	8.86	8.85	+0.0085	-0.00083
		50	69.85	8.81	8.81		
75.84	26.78	0	70.63	8.48	8.48		
		30	70.03	8.56	8.53	+0.0028	-0.00076
		50	68.87	8.51	8.52		
79.69	29.51	0	69.06	8.08	8.09		
		30	68.66	8.18	8.16	+0.0214	-0.0012
		50	67.24	8.10	8.12		

TABLE I (continued).

1.	2.	3.	4.	5.	6.	7.	8.
83.06	32.14	0	67.22	7.70	7.71		
		30	66.72	7.78	7.78	+0.0108	—0.00092
		50	65.47	7.73	7.72		
86.26	34.89	30	64.12	7.36	7.38		
87.29	35.80	0	64.12	7.19	7.19		
		30	63.29	7.23	7.25	—0.0114	—0.00054
		50	62.20	7.19	7.18		
89.29	37.70	0	62.06	6.91	6.92		
		30	61.24	6.94	6.97	—0.0094	—0.00060
		50	60.10	6.90	6.92		
91.82	40.25	30	58.34	6.57	6.60		
92.62	41.09	30	57.53	6.46	6.48		
		50	56.70	6.44	6.46		
93.63	42.20	0	57.06	6.29	6.29		
		30	55.56	6.33	6.33	—0.0083	—0.00044
		50	56.42	6.30	6.30		
94.49	43.16	0	56.18	6.19	6.19		
		30	55.44	6.21	6.18	—0.0165	—0.00028
		50	54.67	6.19	6.20		
95.15	43.89	30	54.68	6.12	6.13		
95.66	44.51	0	54.98	6.05	6.04		
		30	54.28	6.07	6.06	—0.0171	—0.00021
		50	53.61	6.06	6.06		
96.12	45.05	0	54.44	5.99	5.99		
		30	53.67	6.00	6.01	—0.0235	—0.000075
		50	53.08	6.00	6.01		
96.89	45.98	30	52.79	5.90	5.91		
97.32	46.51	30	52.33	5.85	5.86		
99.20	48.92	30	50.23	5.62	5.61		
99.46	49.27	30	50.08	5.61	5.60		
99.80	49.72	30	49.63	5.56	5.56		
		50	49.06	5.56	5.54		
100.00	50.00	30	49.62	5.56	5.52		
100.80		30	49.47		
101.60		30	49.53		
102.40		30	49.62		
102.60		30	49.72		
103.05		30	49.91		
103.10		30	49.98		
103.45		30	50.01		

As it was found impossible to express directly the variation in surface tension with percentage composition at any one temperature, by aid of an equation, various indirect methods were tried which would enable one ultimately to interpolate with accuracy the value of γ at any desired concentration. The method which was finally adopted was one employ-

ing the values of specific cohesion (α^2), which were obtained by aid of the densities of Domke and Bein,¹ from the general equation

$$a_t^2 = \frac{2\gamma_t}{9.80d_t}.$$

The values of a^2 so obtained, when plotted against the molar percentage of SO_3 (i. e., mols of SO_3 per 100 mols of mixture), were found to give a curve which could be broken up into a series of straight lines for interpolation purposes. In this way it is possible to find a^2 at any desired concentration and 0° , 30° or 50° , to calculate from it and the density the corresponding value of γ , and then from the temperature variation of γ (found from the values at the three temperatures) to calculate γ at the desired temperature and concentration.²

The two values of a^2 thus found are given in Columns 5 and 6 of the table, and are included for the reason that only through the variation of a^2 with the composition can values of γ be interpolated at concentrations and temperatures other than those given.

Discussion of the Results.

In Fig. 1 the above results are shown graphically, the ordinates being surface tensions in dynes and the abscissas percentages of sulfuric acid (grams in 100 g. of solution). As will be observed, there is a decided maximum of surface tension in each of the isotherms, which shifts materially in terms of concentration with a change in temperature, and becomes more marked as the temperature increases, showing that the surface tension of all solutions is less influenced by a change in temperature than is that for water. Furthermore, since both the addition of sulfuric acid to water, as well as that of water to sulfuric acid, increases the surface tension, solutions of different concentrations may have the same surface tension value at the same temperature; for example, at 0° , when the concentrations of acid are approximately 28% and 48%, the surface-tensions are identical. In a similar way, the addition of sulfur trioxide to absolute sulfuric acid ($\text{SO}_3\text{-H}_2\text{O}$) also increases its surface tension.

¹ Landolt-Börnstein-Roth, *Tabellen*, 1912, pp. 265-6.

² The equations for this purpose are to be obtained by aid of the following table:

$$a_c^2 = x - \gamma c.$$

(c = mols SO_3 per 100 mols of mixture.)

0°			30°			50°		
Range of c .	x .	γ .	Range of c .	x .	γ .	Range of c .	x .	γ .
0-1.74	15.444	0.601	0.885-3.36	14.457	0.362	1.74-3.36	13.903	0.305
1.74-4.88	15.056	0.377	3.36-6.30	14.156	0.269	3.36-6.30	13.738	0.257
4.88-7.63	14.567	0.274	6.30-16.76	13.755	0.209	6.30-16.76	13.341	0.189
7.63-18.28	14.272	0.238	16.76-26.78	13.062	0.169	16.76-23.18	12.994	0.169
18.28-24.89	13.167	0.177	26.78-43.16	12.446	0.145	23.18-35.80	12.525	0.149
24.89-42.20	12.287	0.142	43.16-48.92	10.606	0.102	35.80-42.20	12.054	0.136
42.20-45.05	10.802	0.107	48.92-49.72	9.354	0.076	42.20-49.72	10.515	0.100

If this curve were examined by one who believes that the property-composition curve can lead to definite information as to the existence of compounds in solutions, he would possibly fix the apparent point of inflection existing at a concentration of about 85% acid as indicating the presence of the hydrate $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. It is true that such a compound

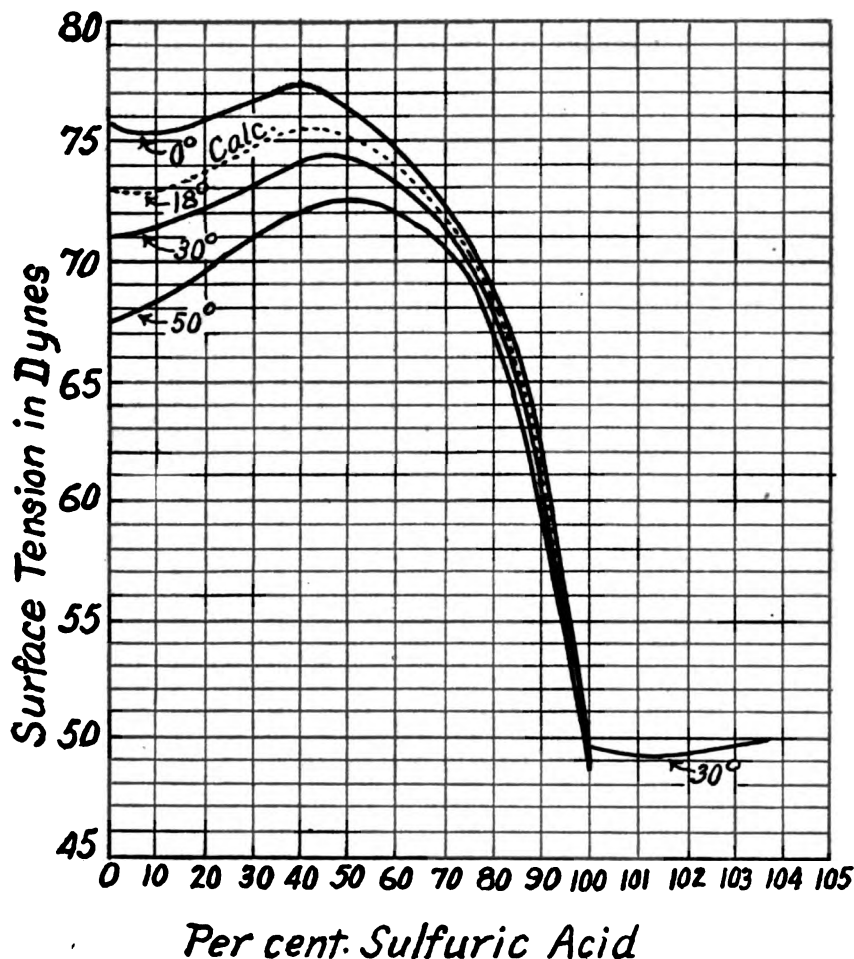


Fig. 1.

is proven to exist by the phase rule, and further, at least one other physical property shows irregularities at this concentration when so treated;¹ but as far as this one curve is concerned the indication must be regarded as altogether too faint for the drawing of any definite conclusion.

In Fig. 2 is presented a graph similar to that given by Röntgen and

¹ See Washburn, *loc. cit.*, p. 407.

Schneider,¹ and showing the relationship between surface tension and compressibility of sulfuric acid-water solutions. Although a direct comparison of our surface-tension results with theirs is impossible, as they employ arbitrary units for the expression of surface tension, the close similarity of the two surface-tension curves can be taken as showing that the results would agree very closely if expressed in the same units. Since their compressibility results are given at 18°, it was necessary for us to interpolate values of γ for that temperature by aid of columns 7 and 8 of Table I; it is from these that our surface-tension curve here is

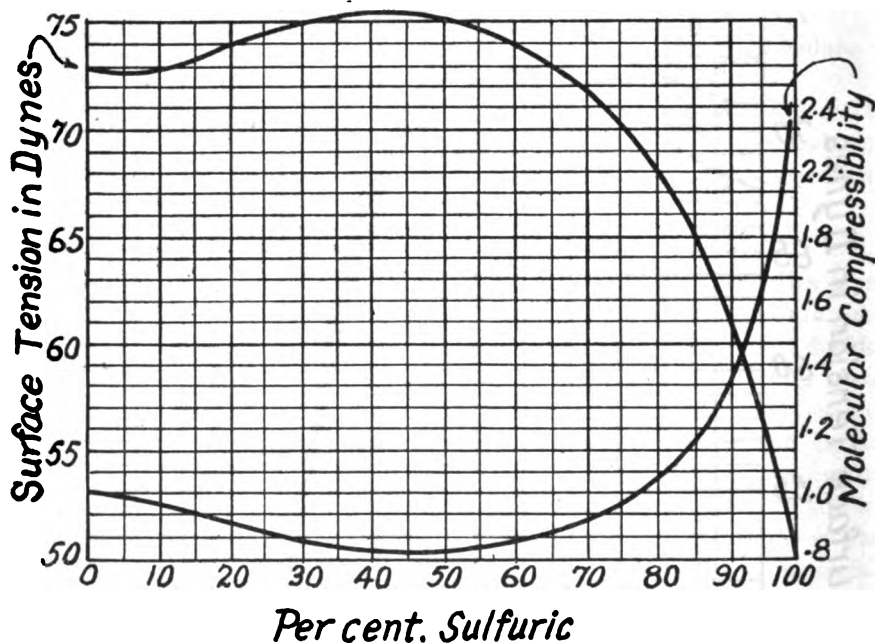


Fig. 2.

made up, and from which the dotted curve in Fig. 1 was plotted. Owing to the artificial unit selected by Röntgen and Schneider for the expression of the compressibility results in their curve, *viz.*, *molecular compressibility*, which is the relative compressibility expressed in terms of water, when the change in volume is measured as taking place, not in equal volumes, but in volumes which contain an equal number of mols, it is difficult to see what significance they hoped to show by the fact that the two curves form such a symmetrical figure, for when plotted in any other terms they show no such relationship.

In Fig. 3 are grouped the curves plotted according to the Denison method,

¹ *Ann. Physik. u. Chem.*, 29, 65 (1886). See also Whatmough, *Z. physik. Chem.*, 39, 165 (1901).

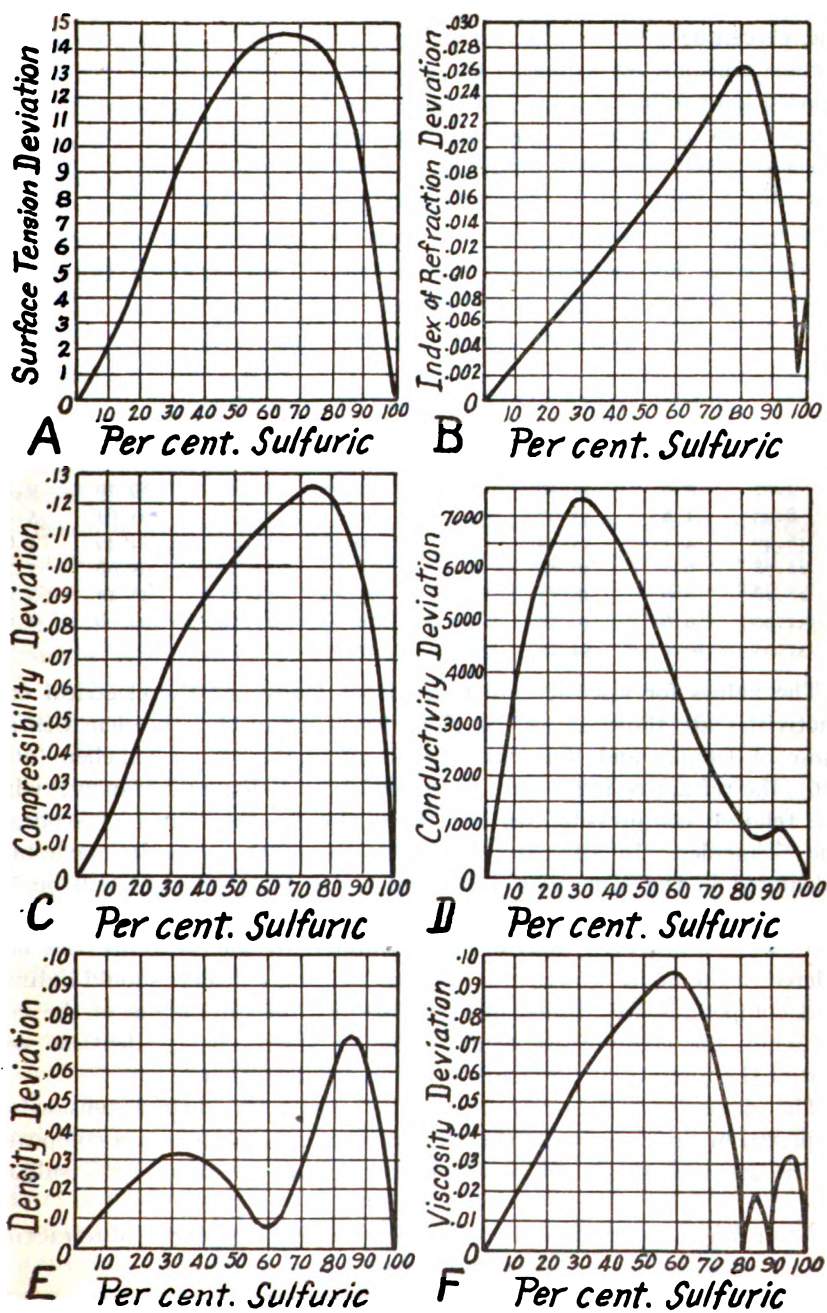


Fig. 3.

using the extents of the deviation from the mixture law as the ordinates, and percentages by weight of the liquid mixture as the abscissas. The surface tensions, according to the mixture law, as stated above, are calculated here from the values of that property for the constituents at the temperature in question, and the proportions in which they are present. Thus for a solution containing 4.67 g. of sulfuric acid to 95.33 g. of water, since the γ values at 0° are, respectively, 50.2 and 75.75 dynes, we have

$$\gamma_{\text{mixt.}} = (0.0467 \times 50.2) + (0.9533 \times 75.75) = 74.55 \text{ dynes.}$$

In this way the deviations shown in Table II are obtained, from which the above curve, A of Fig. 3, is obtained.

TABLE II.—SURFACE-TENSION DEVIATIONS.

Column I gives g. H_2SO_4 per 100 g. of solution. II gives value of γ obs. minus γ calc., where γ calc. is found from the mixture law.

I.	II.	I.	II.	I.	II.	I.	II.
0	0.0	40.71	11.7	57.86	14.2	87.29	10.7
4.67	0.8	42.38	12.2	61.08	14.3	89.29	9.1
8.93	1.8	43.97	12.5	66.23	14.6	93.63	5.2
16.40	4.1	45.53	12.9	70.18	14.4	94.49	4.6
22.78	6.1	46.88	13.0	72.95	14.4	95.66	3.7
28.18	8.0	48.23	13.1	75.84	14.3	96.12	3.2
32.90	9.6	49.51	13.3	79.69	13.7	100.00	0.0
37.05	10.7	54.15	13.9	83.06	12.7

The values for viscosity are taken from Dunstan;¹ the electrical conductivities are those at 18° as given by Kohlrausch;² the densities are those of Domke and Bein³ as reproduced in the above Tabellen (265–266); the refractive indices are those found by Velej and Manley;⁴ while the relative compressibilities are those already mentioned of Röntgen and Schneider. In all cases the deviations of these results have been calculated in the same way as that illustrated above, so it will be unnecessary to present the actual values here.

As will be observed, maxima are exhibited by all the properties considered in the figure which, according to Denison's theory, should indicate that compounds are formed in every case by the interaction of the constituents, the composition of a compound always being identical with that of the mixture at the point of maximum deviation.

The deviation-of-property-composition curve for surface tension interpreted in this way would show the existence in solution of a compound of the formula $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$, which corresponds to about 65% sulfuric acid.

According to the deviation-composition curve for the index of refraction,

¹ *J. Chem. Soc.*, 91, 85 (1907); *Proc. Chem. Soc.*, 30, 104 (1914).

² Landolt-Börnstein-Roth, *Tabellen*, 1912, pp. 1099–1100.

³ *Z. anorg. Chem.*, 43, 125 (1905).

⁴ *Proc. Roy. Soc., (A)* 76, 469–87 (1905).

a compound is indicated in the vicinity of 80%, while 85% would indicate $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ and 73% acid corresponds to $\text{H}_2\text{SO}_4\cdot 2\text{H}_2\text{O}$ —the former composition being indicated by a maximum deviation in the compressibility deviation curve at that point also. The curves for the deviation of the other three properties considered show either two or three maxima each. Those for density indicating compounds of the formula $\text{H}_2\text{SO}_4\cdot 12\text{H}_2\text{O}$ (30% acid) and $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ (85% acid), while conductivity also leads to $\text{H}_2\text{SO}_4\cdot 12\text{H}_2\text{O}$ (30% acid) as well as to $3\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ (94% acid); and, finally viscosity shows its three maxima at $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$ (58% acid), $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ (85% acid) and either $3\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ (94%) as with conductivity, or $4\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ (95%), $5\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ (96%), it is impossible to decide which from the data

It is to be remembered here that the phase rule consideration of this system, SO_3 in water, indicates the existence of the following solid hydrates: $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$, $\text{H}_2\text{SO}_4\cdot 2\text{H}_2\text{O}$, and $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$, only the latter existing as a solid above -15° .

Unless the approximate position of the point of maximum deviation is first found, and later examined very closely, at small concentration intervals, errors in fixing the real maximum point up to perhaps 5% might well be present, which could account for some of the only approximate agreements in concentration noticeable at the maxima above. This would also account for the uncertainty as to which compound is shown by viscosity by the last maximum point considered, and by compressibility.

In connection with the finding of certain compounds indicated by the aid of one physical property, which are not shown by others, Denison calls attention to the fact that the compound formed may well be undistinguishable from the constituents, using one physical property as the criterion, whereas on the basis of some other property, it may vary widely. If this be true, a study of all properties would be necessary to fix all existing compounds.

Whether or not Denison's theory solves the question as to the existence of compounds in mixed liquids, the method does, at any rate, call attention to the various concentrations at which the maximum variation from the mixture law is found, according to which of the various physical properties is selected as a criterion. In this way, at any rate, the contemplated work of this series will call attention to those mixtures which are characteristic in producing the maximum variation from the mixture law, *i. e.*, will determine those mixtures which are most abnormal, so that in time, perhaps, not only will it be possible to prove the Denison theory to be correct or incorrect, but in the latter case, by a statistical study, to make an equivalent step forward in answering the question as to what happens when two liquids are mixed.

Summary.

The results of this research may be summarized briefly as follows:

(1) More than one hundred determinations of the surface tension of forty-eight concentrations of sulfuric acid in water, at various temperatures, have been made by aid of the drop-weight method, and formulas provided by which the surface tension and specific cohesion can be calculated at any concentration and temperature between 0° and 50° . A method is also given which obviates any difficulty produced in the drop-weight method by high viscosity and poor covering power.

(2) It is found that both the addition of sulfuric acid to water, as well as that of water to sulfuric acid, causes an increase in the surface tension, so that different concentrations of sulfuric acid may have identical surface-tension values at the same temperature. The addition of SO_2 to sulfuric acid ($\text{SO}_2 \cdot \text{H}_2\text{O}$) also increases the surface tension.

(3) If the property-composition curve means anything as to chemical interaction, it can be assumed, perhaps, from the surface-tension results to indicate the existence of the hydrate $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ at 85% acid.

(4) The application of the theory of Denison, that the deviation of a property from the mixture law plotted against the composition, shows at the point of maximum deviation the presence of a compound identical in composition with that of the solution leading to that maximum deviation, indicates the following hydrates in water solutions of sulfuric acid, according to the property which is taken as a criterion:

$\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ by density, compressibility viscosity (and refraction);

$\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ (by refraction);

$\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ by surface tension;

$3\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ by conductivity (and viscosity);

$\text{H}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$ by conductivity and density;

$4\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ or $5\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (by viscosity).

NEW YORK CITY.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON, D. C.]

THE TERNARY SYSTEM $\text{CaO}-\text{Al}_2\text{O}_3-\text{MgO}$.

BY G. A. RANKIN AND H. E. MERWIN.

Received January 21, 1916.

The study of a three-component system can be undertaken only if the equilibrium relations in the three systems of two components have previously been ascertained, a prerequisite of which again is that the properties of the pure components be adequately known. Similarly, before one can proceed to the investigation of a four-component system—at least with the hope of a successful outcome—one must have elucidated the equilibrium relations in the four possible systems made up of combinations

of three of the components. The study of the important system of the oxides CaO , Al_2O_3 , SiO_2 , MgO has reached the point that two of the ternary systems have now been completed; the results obtained on the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ were published recently,¹ while the present paper is a record of the study of the system $\text{CaO-Al}_2\text{O}_3\text{-MgO}$.² The present system has involved no problem as interesting as that of the constitution of Portland cement clinker, a knowledge of which was one of the results of the work on the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$; nevertheless it was necessary to work this system out, since the relation in any ternary system cannot be deduced by analogy with any similar system, but can only be learned by experiment. In this system, as it happens, the substances stable in contact with melts containing only the three components include no ternary compounds, and are only eight in number (inclusive of the components themselves) whereas in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system the corresponding number is fourteen.

In the following pages we discuss the equilibrium relations of the several crystalline phases which separate from anhydrous melts containing only the oxides CaO , Al_2O_3 , MgO —in other words, the solubility of the several solid phases in such liquids. These relations have been ascertained, by means of determinations of melting temperatures and optical characteristics of the components and compounds, throughout the range of concentrations within which they occur as stable solid phases. The general principles upon which the mode of experiment is based, as well as most of the actual methods employed, have been fully described in a previous paper, to which the reader is referred.³

One paper dealing with the three binary systems⁴ has already been published. In the present paper we are able to give some new data on the systems $\text{MgO-Al}_2\text{O}_3$ and CaO-MgO .

The Components and Binary Systems.

In presenting the results obtained from a study of the components and binary systems, we will consider only such new data as has not already been published. This will include a study of the component MgO , a new form of the component Al_2O_3 , and the binary systems MgO-CaO and $\text{MgO-Al}_2\text{O}_3$. The results obtained from the study of CaO and the system $\text{CaO-Al}_2\text{O}_3$ are given in the previous paper.

Magnesia, MgO .—The melting point of MgO as determined by

¹ Rankin and Wright, *Am. J. Sci.*, [4] 39, 1 (1915).

² A portion of the system CaO-MgO-SiO_2 has also been investigated already. See paper by N. L. Bowen, "The Ternary System Diopside-Forsterite-Silica," *Am. J. Sci.*, [4] 38, 207 (1914).

³ Rankin and Wright, *Am. J. Sci.*, [4] 39, 1 (1915), referred to hereafter as the previous paper.

⁴ *Am. J. Sci.*, [4] 28, 293 (1909).

Kanolt is 2800° .¹ No indications of a second form have so far been observed.

In silicate melts MgO crystals are not faceted,² but with CaO and Al_2O_3 present sharply bounded and skeletal octahedrons, sometimes modified by the cube, were seen frequently.

Alumina, Al_2O_3 .—This investigation has shown that alumina occurs in two distinct forms: (1) α - Al_2O_3 (artificial corundum) is the only form which has previously been described; the melting point of this form as determined by Kanolt is 2050° ;³ (2) β , the new form of alumina, is found to occur occasionally in charges of pure alumina which have been melted and slowly cooled. Having once formed, it has not been found possible to cause this β form to revert to the α form, even when held at temperatures above or below that required for melting. The presence of a small amount of MgO (0.5%) materially assists the formation of this new form, while melted alumina containing small amounts of either CaO or SiO_2 when cooled has been found to crystallize as the α form (corundum). It would appear therefore that β - Al_2O_3 may be monotropic with respect to the α form, although the exact relation existing between these two forms is uncertain by reason of the experimental difficulties involved in investigations requiring such extremely high temperature.

β - Al_2O_3 is hexagonal, often appearing in groups of over-lapping triangular plates with perfect basal cleavage. The refractive index ϵ appears to vary, even in preparations made from our purest alumina, due account being taken of the difficulty of getting properly oriented sections. The values found are 1.635 to 1.650. In the same preparations ω was 1.677 ± 0.003 . In preparations containing MgO, ϵ may be as low as 1.629, and ω may vary between 1.665 and 1.680. But no relation between the content of MgO in the melt and the refractive index of the crystals has appeared.

Some artificial alumina⁴ abrasives have been found to contain small amounts of this β - Al_2O_3 having $\epsilon = 1.631$ and $\omega = 1.674$.

The Binary System: Lime-Magnesia.—It was found that in all fused mixtures of CaO and MgO the two oxides crystallize out side by side, showing no evidence of combination, that is, there is no compound formed stable in contact with melt. The concentration temperature diagram for the system CaO-MgO is given in Fig. 1. The melting points of CaO and MgO are taken as 2570° and 2800° , respectively, the values determined by Kanolt at the Bureau of Standards. The eutectic, as obtained

¹ Kanolt, *J. Wash. Acad. Sci.*, 3, 315 (1913).

² Anderson, *Am. J. Sci.*, [4] 39, 421 (1915).

³ *J. Wash. Acad. Sci.*, 3, 315 (1913).

⁴ β - Al_2O_3 separated from an artificial alumina abrasive was analyzed by H. S. Washington and found to have the chemical composition Al_2O_3 ; its density is 3.30 ± 0.01 .

by extrapolation of the $\text{CaO}-\text{MgO}$ boundary in the ternary system $\text{CaO}-\text{Al}_2\text{O}_3-\text{MgO}$, has the approximate composition 67% CaO , 33% MgO and its melting point is $2300^\circ \pm 50^\circ$.

The Binary System: Magnesia - Alumina.

— MgO and Al_2O_3 combine to form but a single compound, $\text{MgO} \cdot \text{Al}_2\text{O}_3$ (MgO 28.4%, Al_2O_3 71.6%). This compound is stable at its melting point, which is $2135^\circ \pm 20^\circ$. With MgO , $\text{MgO} \cdot \text{Al}_2\text{O}_3$ forms a eutectic of the composition MgO 45%, Al_2O_3 55%; its melting point is $2030^\circ \pm 20^\circ$.

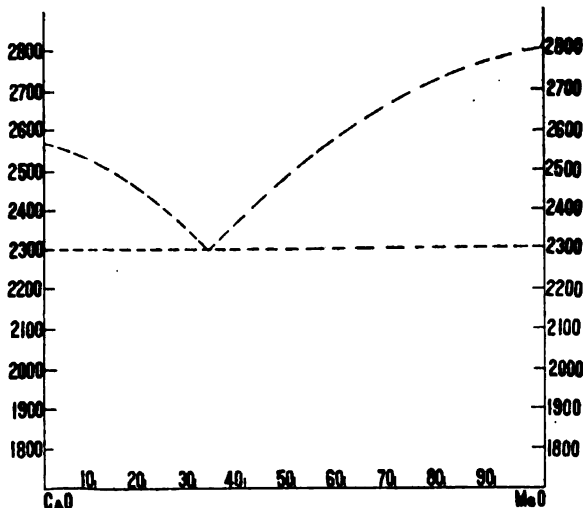


Fig. 1.—Concentration-temperature diagram for the system lime-magnesia.

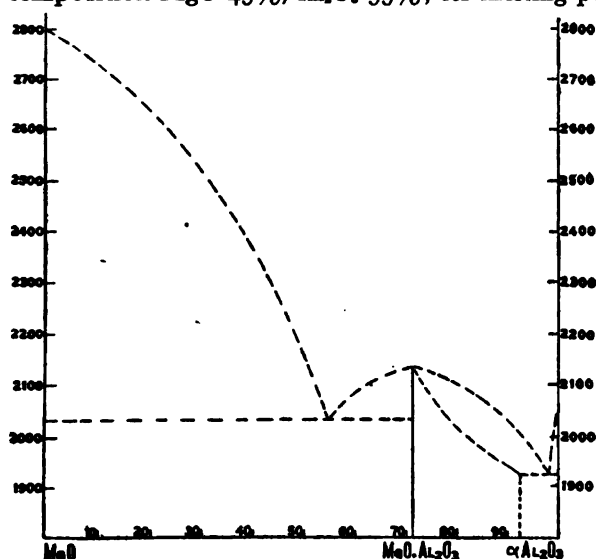


Fig. 2.

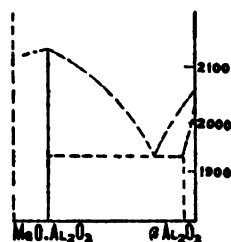


Fig. 2a.

Fig. 2.—Concentration-temperature diagram for the system magnesia-alumina.

Fig. 2a.—Concentration-temperature diagram for the system spinel-alumina.

It was found exceedingly difficult to establish definitely the relations existing between the compound $\text{MgO} \cdot \text{Al}_2\text{O}_3$ and the two forms of Al_2O_3 . This is due to the fact that since $\beta\text{-Al}_2\text{O}_3$ is apparently monotropic with

respect to the α form, it is not possible to define conditions for the preparation of melts which on cooling will crystallize to give $\text{MgO} \cdot \text{Al}_2\text{O}_3$ and the desired form of Al_2O_3 . However from the optical examination of the crystals which have separated in a large number of experiments, it appears that the compound $\text{MgO} \cdot \text{Al}_2\text{O}_3$ forms with $\alpha\text{-Al}_2\text{O}_3$ a nearly complete series of solid solutions, but with $\beta\text{-Al}_2\text{O}_3$ it does not enter into solid solution except that the $\beta\text{-Al}_2\text{O}_3$ seems to take a limited amount of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ in solid solution. Nevertheless, one cannot predict which alternative will happen in any particular case; for under apparently identical conditions of melting and cooling sometimes the solid solution will be formed, sometimes the $\text{MgO} \cdot \text{Al}_2\text{O}_3$ along with the $\beta\text{-Al}_2\text{O}_3$. These relations are represented by concentration-temperature diagrams; Fig. 2, that for the system $\text{MgO}-\alpha\text{-Al}_2\text{O}_3$ and Fig. 2a, that for the system $\text{MgO}-\text{Al}_2\text{O}_3-\beta\text{-Al}_2\text{O}_3$. In these diagrams the melting temperatures for the various mixtures are represented by dotted lines, for the reason that no satisfactory melting temperatures could be obtained except for pure MgO — 2800° ; pure $\text{MgO} \cdot \text{Al}_2\text{O}_3$ — $2135^\circ \pm 20^\circ$; pure Al_2O_3 — $2050^\circ \pm 20^\circ$; the eutectic $\text{MgO}-\text{MgO} \cdot \text{Al}_2\text{O}_3$ (45% MgO , 55% Al_2O_3)— $2030^\circ \pm 20^\circ$; the eutectic $\alpha\text{-Al}_2\text{O}_3\text{-MgO} \cdot \text{Al}_2\text{O}_3$ (98% Al_2O_3 , 2% MgO)— $1925^\circ \pm 40^\circ$; and the eutectic $\beta\text{-Al}_2\text{O}_3\text{-MgO} \cdot \text{Al}_2\text{O}_3$ (92% Al_2O_3 , 8% MgO)— $1925^\circ \pm 40^\circ$.

The Optical Properties of the crystals separating in the different parts of the spinel field are not very different from those of pure spinel, although some of these crystals do not contain more than 8% of theoretical spinel. For example, from the melt Al_2O_3 98%, MgO 2% there separated about 90% spinel and 10% of the two forms of Al_2O_3 . The refractive index, n , of this spinel was 1.733. From another melt spinel containing its own weight of dissolved alumina had a refractive index of 1.726. A practically pure spinel made in the iridium furnace¹ had $n = 1.718 \pm 0.002$. The mean refractive index of $\alpha\text{-Al}_2\text{O}_3$ (corundum) is 1.765 and of $\beta\text{-Al}_2\text{O}_3$ is about 1.665. Thus the refractive index of spinel crystals of intermediate composition is not even an approximate additive function of the refractive indices of two end members. Such a relation might, however, exist if both forms of Al_2O_3 are dissolved in the same spinel crystal. The spinel is strictly isotropic unless the alumina is greatly in excess, in which case double refraction appears and increases with the content of alumina to perhaps 0.003. The value is hard to estimate for the grains then contain a fine, irregular lattice which extinguishes as a unit, and the elements of which seem to extend in three rectangular directions.

The Identification of Spinel in Presence of Periclase was found to be im-

¹ A similar preparation melted in the arc furnace had $n = 1.723 \pm 0.002$. *Am. J. Sci.*, 28, 326 (1909).

practicable by an optical method alone owing to their being isotropic and similar in refractive index, and often having the same crystal habit. Spinel—unless in the process of dissolving—always appeared in faceted or skeleton octahedra; periclase appeared in rounded grains as well as in the same habits as spinel. In cases of doubt in identification, the powdered preparation was warmed on the slide with a few drops of mixed nitric and hydrochloric acids diluted with an equal amount of water. The glasses, containing the crystals, and the periclase dissolved leaving the spinel. By interrupting the process of solution partly dissolved grains of periclase could be identified.

The Binary System: Lime-Alumina.—The results obtained from the investigation of this system have already been published. Some new optical data, however, have been obtained for two of the calcium aluminates as they occur in ternary mixtures of CaO , Al_2O_3 , MgO . The compound $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ was here observed in skeleton tetrahedrons. The compound $\text{CaO} \cdot \text{Al}_2\text{O}_3$ was seldom twinned in these preparations while in silicate mixtures it was almost invariably twinned. The value of $2V$ of this compound in silicate preparations is given at 36° ; variations to nearly uniaxial were observed during this investigation. Besides irregular grains and fibers many crystals which appeared to be orthorhombic were observed. No variations in refractive index from crystals found in the silicate melts were noted.

The Ternary System $\text{CaO}-\text{Al}_2\text{O}_3-\text{MgO}$.

The results obtained from the investigation of the three binary systems show that in the study of the ternary system we must delimit the regions of stability of the three components CaO , Al_2O_3 , MgO ; the five binary compounds $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, $\text{CaO} \cdot \text{Al}_2\text{O}_3$, $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$, $\text{MgO} \cdot \text{Al}_2\text{O}_3$, and in addition to these any other compounds, binary or ternary, which may be stable in contact with melt. As a matter of fact, in the present system no substances other than those already encountered in the binary system appear.

The first step in this investigation consisted in the preparation of charges whose compositions represented random intervals over the entire range of ternary mixtures. The primary crystalline phase was then determined for each of these charges which could be quenched at some temperature below 1600° in such a way that a single crystalline phase imbedded in glass could be obtained. From this preliminary reconnaissance we located approximately the fields with their limiting boundary curves and quintuple points. With these general data as a basis, other intermediate charges were prepared and their primary phases determined; this secured a more exact location of the boundary curves and quintuple points, the compositions along boundary curves (lines) being accurate to within

TABLE I.

Quenchings Which Determine the Limits of the Field of CaO.

Phases present, glass + CaO.

Composition wt. %.			Temp.	Time in hours.
CaO.	Al ₂ O ₃ .	MgO.		
55	42	3	1525°	0.25
53	41	6	1460°	0.5
52	42	6	1480°	0.5
62	37	7	1450°	1.0
53	39	8	1550°	0.25
55	35	10	1570°	0.5

TABLE II.

Quenchings Which Determine the Limits of the Field of 3CaO.Al₂O₃.

Phases present, glass + 3CaO.Al₂O₃.

Composition wt. %.			Temp.	Time in hours.
CaO.	Al ₂ O ₃ .	MgO.		
54	43	3	1480°	0.25
48	48	4	1378°	0.5
51	43	6	1435°	0.25
47	47	6	1360°	1.0

TABLE III.

Quenchings Which Determine the Limits of the Field of 5CaO.3Al₂O₃.

Phases present, glass + 5CaO.3Al₂O₃.

Composition wt. %.			Temp.	Time in hours.
CaO.	Al ₂ O ₃ .	MgO.		
48	50	2	1410°	0.5
48	48.5	5.5	1370°	0.5
42.5	51.5	6	1370°	0.5
44.5	49	6.5	1400°	0.25

TABLE IV.

Quenchings Which Determine the Limits of the Field of CaO.Al₂O₃.

Phases present, glass + CaO.Al₂O₃.

Composition wt. %.			Temp.	Time in hours.
CaO.	Al ₂ O ₃ .	MgO.		
35.2	62	2.8	1550°	0.25
45	52	3.0	1390°	0.5
34	63	3.0	1560°	0.25
37	58.5	4.5	1515°	0.5
42	53	5	1400°	0.5
42	52	6	1360°	0.5
41	53	6	1375°	0.5

TABLE V.

Quenchings Which Determine the Limits of the Field of 3CaO.5Al₂O₃.

Phases present, glass + 3CaO.5Al₂O₃.

Composition wt. %.			Temp.	Time in hours.
CaO.	Al ₂ O ₃ .	MgO.		
33	64.5	2.5	1590°	0.25
32	65	3	1585°	0.5
30.5	66	3.5	1600°	0.25

TABLE VI.

Quenchings Which Determine the Limits of the Field of MgO.Al₂O₃.

Phases present, glass + MgO.Al₂O₃.

Composition wt. %.			Temp.	Time in hours.
CaO.	Al ₂ O ₃ .	MgO.		
33.5	63.5	3	1563°	0.25
32	64	4	1570°	0.25
30.5	65.5	4	1610°	0.25
34.5	61	4.5	1545°	0.5
30	64	6	1585°	0.5
40	53	7	1400°	0.5
37	53	10	1500°	0.25
34	54	12	1575°	0.25

TABLE VII.

Quenchings Which Determine the Limits of the Field MgO.

Phases present, glass + MgO.

Composition wt. %.			Temp.	Time in hours.
CaO.	Al ₂ O ₃ .	MgO.		
50	43.5	6.5	1435°	0.5
45.5	48	6.5	1375°	0.5
51.7	41.3	7	1465°	0.5
48	45	7	1400°	0.5
46	47	7	1375°	2.0
44	49	7	1375°	0.5
42.5	50.5	7	1355°	2.5
41	52	7	1375°	0.5
51.5	40.5	8	1500°	0.5
45	47	8	1500°	0.25
43	49	8	1450°	0.5
52	39.5	8.5	1550°	2.5
52.5	37.5	10	1610°	0.25
50	40	10	1465°	0.5
45	45	10	1600°	0.25
40	50	10	1425°	1.5
35	52.5	12.5	1580°	0.25
45	40	15	1430°	0.5
45	35	20	1500°	0.5
35	45	20	1400°	0.5
35	30	35	1550°	0.25

TABLE VIII.
Quenchings Which Determine the Limits of the Field of $\beta\text{-Al}_2\text{O}_3$.
Phases present, glass + Al_2O_3 .

Composition wt. %.			Temp.	Time in hours.
CaO.	Al_2O_3 .	MgO.		
20	75	5	1700 ¹	0.25

$\pm 1.0\%$, and quintuple compositions being accurate within a radius of 0.5% .

The data obtained in this way are given in Tables I-VIII. Each of these tables contains the data for the location of the boundaries and quintuple points which delimit the field for one crystalline phase. The limits

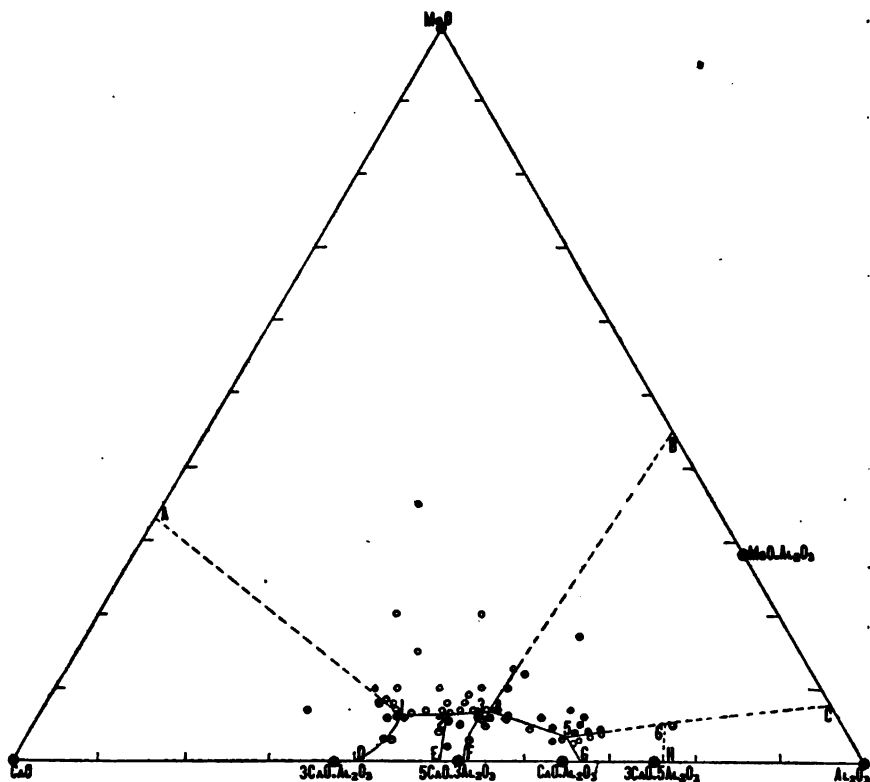


Fig. 3.—Projection of concentration-temperature diagram for the ternary system $\text{CaO}-\text{Al}_2\text{O}_3-\text{MgO}$, giving compositions whose primary phases determined the location of boundary curves and quintuple points.

of the field of stability, as determined by these data, are represented in the triangular diagram, Fig. 3. The dots given in the diagram represent the compositions examined.

¹ Heated in iridium furnace.

When the compositions within each field, along each boundary curve and at each quintuple point are known it is still necessary to determine the composition of each unknown crystalline phase and the equilibrium temperature within the fields, along the boundary curves and at each quintuple point. Examination of Fig. 3 shows that there are no crystalline phases not found in the binary series, *i. e.*, that there are no ternary compounds stable in contact with the melts; altogether, therefore, there are 8 fields, 13 boundary curves and 6 quintuple points.

The Fields.

In the complete $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ diagram there proved to be 8 separate fields of stability; that is, there are 8 separate regions—one for each chemical compound (including the original components) which occurs in the system—within which a single particular compound is in equilibrium with solution and vapor. Each field may be regarded as the solubility region of a single compound in solutions of two other definite compounds or the melting region of a single compound in solutions of three definite compounds.

The melting temperatures within each field are obtained by quenching to determine the temperature above which glass (liquid) is obtained and below which a single crystalline phase is obtained imbedded in glass, as determined by optical examination with the microscope. By this method of procedure it is possible to determine melting temperatures up to 1600° —the limit of the platinum resistance furnace in which quenchings are made.

We shall now consider the fields separately, the numbers and letters used to designate them being those given in Fig. 3. Examination of Fig. 3 shows that the field of each of several of the compounds of CaO and Al_2O_3 covers approximately the same area that it did in the equilibrium diagram for CaO , Al_2O_3 and SiO_2 . This is merely a strange coincidence which could not be predicted, since the solubility of a compound in one series of ternary solutions is not necessarily the same as for any other series of ternary solutions.

1. **The field of lime** $(\text{CaO})(\text{D-1-A-CaO})$.—Practically all the melting temperatures within this field are too high for determination, and hence the slope of its melting surface was deduced from the melting temperature of the boundaries.

2. **The field of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ (D-1-2-E).**— $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ is a compound unstable at its melting point, wherefore its composition lies outside of its field of stability. Table IX gives the quenchings which determine the melting temperature of various compositions within this field.

3. **The field of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ (E-2-3-F).**— $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ occurs in two forms, a stable form and an unstable form which occurs in melts with considerable frequency. The melting slope of the narrow field for the stable

form follows from the melting temperature of the boundaries which have been ascertained.

TABLE IX.

Quenchings Which Determine Melting Temperature¹ of Various Compositions within Field D-1-2-E; Primary Phase is $3\text{CaO}.\text{Al}_2\text{O}_3$.

Composition wt. %.			Temp.	Time in hours.	Phases present.
CaO.	Al_2O_3	MgO.			
54	43	3	1490°	0.25	Glass
			1480°	0.25	Glass + $3\text{CaO}.\text{Al}_2\text{O}_3$
48	48	4	1385°	1.0	Glass
			1378°	0.5	Glass + $3\text{CaO}.\text{Al}_2\text{O}_3$
51	46	6	1450°	0.5	Glass
			1435°	0.25	Glass + $3\text{CaO}.\text{Al}_2\text{O}_3$

4. The field of $\text{CaO}.\text{Al}_2\text{O}_3$ (F-3-4-5-G).—Table X gives the quenchings which determine the melting temperatures of various compositions within this field.

TABLE X.

Quenchings Which Determine Melting Temperature of Various Compositions within Field F-3-4-5-G; Primary Phase is $\text{CaO}.\text{Al}_2\text{O}_3$ (m. p. $1600^\circ \pm 5^\circ$).

Composition wt. %.			Temp.	Time in hours.	Phases present.
CaO.	Al_2O_3	MgO.			
35.2	62	2.8	1560°	0.25	Glass
			1550°	0.25	Glass + $\text{CaO}.\text{Al}_2\text{O}_3$
45	52	3	1395°	0.5	Glass
			1390°	0.5	Glass + $\text{CaO}.\text{Al}_2\text{O}_3$
42	52	6	1390°	0.5	Glass
			1360°	0.5	Glass + $\text{CaO}.\text{Al}_2\text{O}_3$

5. The field of $3\text{CaO}.5\text{Al}_2\text{O}_3$ (G-5-6-H).— $3\text{CaO}.5\text{Al}_2\text{O}_3$ occurs in two forms, a stable form and an unstable form, which is occasionally found in melts. Practically all the melting temperatures within this field are too high for determination, and hence the melting surface was deduced from the melting temperatures of the boundaries.

6. The field of alumina (Al_2O_3) (H-6-C- Al_2O_3).—All the melting temperatures within this field are too high for determination and hence the slope of its melting surface was deduced from the melting temperature of its boundaries.

7. The field of $\text{MgO}.\text{Al}_2\text{O}_3$ (B-4-5-6-C).—Most of the melting tempera-

¹ The melting temperatures, given in this table and those which follow for fields and boundary curves, were not determined with the greatest possible accuracy, for two reasons: (1) It was possible to establish the equilibrium relations in this system with approximate determinations of these temperatures. (2) The essential points (quintuple points) in this system are all contained within a small area of compositions, so that the accurate determination of the melting temperature of each of these points, together with the melting temperatures of pure compounds and quadruple points, enables one to give rather accurately the melting slopes of the various ternary fields and boundary curves.

tures within this field are too high for determination; those of certain compositions are given in Table XI.

TABLE XI.

Quenchings Which Determine Melting Temperatures of Various Compositions within Field B-4-5-6-C; Primary Phase is $\text{MgO} \cdot \text{Al}_2\text{O}_3$ (m. p. $2135^\circ \pm 20^\circ$).

Composition wt. %.			Temp.	Time in hours.	Phases present.
CaO.	Al ₂ O ₃ .	MgO.			
37	53	10	1525°	0.25	Glass
			1500°	0.25	Glass + $\text{MgO} \cdot \text{Al}_2\text{O}_3$
34	54	12	1610°	0.25	Glass
			1575°	0.25	Glass + $\text{MgO} \cdot \text{Al}_2\text{O}_3$

8. The field of magnesia (MgO) (A-1-2-3-4-B- MgO).— MgO , which occurs in but a single form, is the primary crystalline phase for over one-half of the area of compositions of CaO , Al_2O_3 , MgO , represented in Fig. 3. Most of the melting temperatures within this area (field) are too high for determination. Those of certain compositions determined by quenching are given in Table XII.

TABLE XII.

Quenchings Which Determine Melting Temperatures of Various Compositions within Field A-1-2-3-4-B- MgO ; Primary Phase is MgO (m. p. 2800°).

Composition wt. %.			Temp.	Time in hours.	Phases present.
CaO.	Al ₂ O ₃ .	MgO.			
51.5	40.5	8	1500°	0.5	Glass + MgO
			1540°	0.5	Glass
45	47	8	1450°	0.25	Glass + MgO
			1500°	0.25	Glass
43	49	8	1450°	0.25	Glass + MgO
			1500°	0.25	Glass
40	50	10	1510°	0.5	Glass + MgO
			1535°	0.5	Glass

The Boundary Curves.

A boundary curve is the line which separates two fields and represents the temperatures and concentrations at which the solid phase of one field is in equilibrium with the solid phase of the other field in coexistence with solution and vapor.

The boundary lines in Fig. 3 represent the projection upon the horizontal plane of the lines on the concentration-temperature solid model. In order to make clear the way in which the temperature varies along these lines, we have made projections upon a vertical plane, obtaining in this way the series of boundary curves reproduced in Fig. 4, in which the numbers and letters used correspond to those in Fig. 3. The ordinates represent temperatures, which were determined experimentally.

These temperatures are ascertained by quenching to determine the temperature above which one solid crystalline phase is obtained im-

bedded in glass and below which two crystalline phases are obtained imbedded in glass, as observed by the microscope. Data obtained in this way giving the temperatures determined for points on the boundaries,

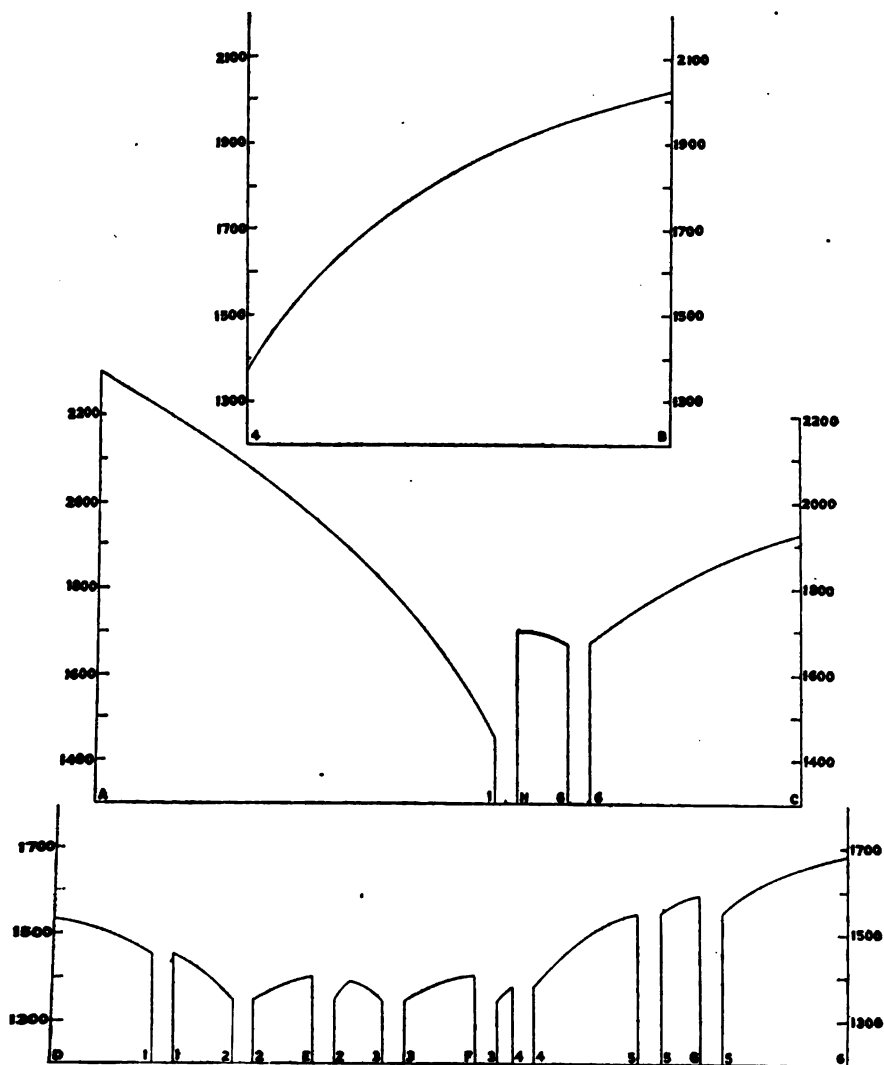


Fig. 4.—Temperature-concentration diagram of the 13 boundary curves which fix the limits of the fields within the ternary system $\text{CaO}-\text{Al}_2\text{O}_3-\text{MgO}$.

are contained in Table XIII. The temperatures at the ends of the boundary curves are given later as quintuple and quadruple point temperatures.

TABLE XIII.

Quenchings Which Determine Temperatures for Points on the Boundary Curves.

Composition wt. %.			Temp.	Time in hours.	Phases present.	Boundary.
CaO.	Al ₂ O ₃ .	MgO.				
55	42	3	1465°	0.5	Glass + 3CaO.Al ₂ O ₃	D-1
			1500°	0.25	Glass + 3CaO.Al ₂ O ₃ + CaO	
48	48	4	1378°	0.5	Glass + 3CaO.Al ₂ O ₃	E-2
			1375°	1.0	Glass + 3CaO.Al ₂ O ₃ + 5CaO.3Al ₂ O ₃	
52	39.5	8.5	1550°	0.25	Glass + MgO	I-A
			1510°	0.5	Glass + MgO + CaO	
52.5	37.5	10	1610°	0.25	Glass + MgO	
			1590°	0.25	Glass + MgO + CaO	
48	45	7	1400°	0.5	Glass + MgO	I-2
			1380°	0.5	Glass + MgO + 3CaO.Al ₂ O ₃	
44.5	49	6.5	1400°	0.25	Glass + 5CaO.3Al ₂ O ₃	2-3
			1360°	0.5	Glass + 5CaO.3Al ₂ O ₃ + MgO	
45	52	3	1390°	0.5	Glass + CaO.Al ₂ O ₃	F-3
			1375°	0.5	Glass + CaO.Al ₂ O ₃ + 5CaO.3Al ₂ O ₃	
42	52	6	1360°	0.5	Glass + CaO.Al ₂ O ₃	
			1350°	1.0	Glass + CaO.Al ₂ O ₃ + 5CaO.3Al ₂ O ₃	
41	52	7	1375°	0.5	Glass + MgO	3-4
			1365°	0.5	Glass + MgO + CaO.Al ₂ O ₃	
34	54	12	1520°	0.5	Glass + MgO.Al ₂ O ₃	4-B
			1475°	0.5	Glass + MgO + MgO.Al ₂ O ₃	
35	52	12.5	1580°	0.25	Glass + MgO	
			1550°	0.25	Glass + MgO + MgO.Al ₂ O ₃	
37	53	10	1500°	0.25	Glass + MgO.Al ₂ O ₃	
			1475°	1.5	Glass + MgO.Al ₂ O ₃ + MgO	
37	58.5	45	1515°	0.5	Glass + CaO.Al ₂ O ₃	4-5
			1485°	0.5	Glass + CaO.Al ₂ O ₃ + MgO.Al ₂ O ₃	
40	53	7	1400°	0.5	Glass + MgO.Al ₂ O ₃	
			1385°	0.5	Glass + MgO.Al ₂ O ₃ + CaO.Al ₂ O ₃	
30.5	65.5	4	1610°	0.25	Glass + MgO.Al ₂ O ₃	5-6
			1600°	0.25	Glass + MgO.Al ₂ O ₃ + 3CaO.5Al ₂ O ₃	

The Quintuple Points.

A quintuple point, a common point for three boundaries, is the point at which three solid phases are in equilibrium with solution and vapor. A quintuple point is known as a eutectic if it is the lowest temperature of the three boundaries of which it is a common point.

The temperature of a quintuple point may be determined in any mixture of the solid phases present at that quintuple point, either from heating curves or quenches to determine the temperature above which two crystalline phases are obtained imbedded in glass (liquid) and below which three solid crystalline phases are obtained; that is, the temperature at which glass first appears in a ternary mixture is the temperature of the quintuple point for that mixture.

Following is a list of the 6 quintuple points giving compositions in weight percentages of CaO, Al₂O₃, MgO and the corresponding temperatures

determined both by heating curves and quenches. The numbers assigned to each quintuple point correspond to the numbers in Fig. 3.

Point 1 is the quintuple point for CaO , MgO and $3\text{CaO}.\text{Al}_2\text{O}_3$ (CaO 51.5, Al_2O_3 43.3, MgO 6.2). Its melting temperature ($1450^\circ \pm 5^\circ$) is based on the values obtained from various compositions as given in Table XIV.

TABLE XIV.

Melting Temperature: Quintuple 1 for CaO , MgO , and $3\text{CaO}.\text{Al}_2\text{O}_3$ as Determined from Various Compositions.

Composition, wt. %	{					
	$\text{CaO} \dots\dots$	52.5	55	52	51.7	50
	$\text{Al}_2\text{O}_3 \dots\dots$	37.5	35	35	41.3	40
Temperature.....	$\text{MgO} \dots\dots$	10.0	10	20	6	7
						10
		1446	1450	1449	Quench	Quench
		1449	1450	1450	1460	1455
		1445	1450	1449
		1447	1450	1446
		1449	1450
Mean,		1447	1450	1449	1460	1455
						1450

Point 2 is the eutectic point for MgO , $3\text{CaO}.\text{Al}_2\text{O}_3$ and $5\text{CaO}.3\text{Al}_2\text{O}_3$ (CaO 51, Al_2O_3 42.7, MgO 6.3). Its melting point $1345^\circ \pm 5^\circ$ is based on the values obtained from compositions given in Table XV.

TABLE XV.

Melting Temperature: Eutectic 2 for MgO , $3\text{CaO}.\text{Al}_2\text{O}_3$ and $5\text{CaO}.3\text{Al}_2\text{O}_3$ as Determined from Various Compositions.

Composition, wt. %	{		
	$\text{CaO} \dots\dots$	45	50
	$\text{Al}_2\text{O}_3 \dots\dots$	35	43.5
Temperature.....	$\text{MgO} \dots\dots$	20	6.5
			10.0
		1340° Quench	1350° Quench
			1340° Quench

Point 3 is the eutectic for MgO , $5\text{CaO}.3\text{Al}_2\text{O}_3$ and $\text{CaO}.\text{Al}_2\text{O}_3$ (CaO 41.5, Al_2O_3 51.8, MgO 6.7). Its melting temperature is $1345 \pm 5^\circ$.

Point 4 is the quintuple point for MgO , $\text{MgO}.\text{Al}_2\text{O}_3$ and $\text{CaO}.\text{Al}_2\text{O}_3$ (CaO 40.7, Al_2O_3 52.4, MgO 6.9). Its melting temperature, $1370 \pm 5^\circ$, is based on the values obtained from various compositions as given in Table XVI.

TABLE XVI.

Melting Temperature: Quintuple Point 4 for $\text{MgO} + \text{MgO}.\text{Al}_2\text{O}_3 + \text{CaO}.\text{Al}_2\text{O}_3$ as Determined from Various Compositions.

Composition, wt %	{				
	$\text{CaO} \dots\dots\dots$	39	31	35	40
	$\text{Al}_2\text{O}_3 \dots\dots\dots$	55	62	52.5	53
Temperature.....	$\text{MgO} \dots\dots\dots$	6	7	12.5	7
					12
		1373	1371	1370	1370
		1374	1373	Quench	Quench
		1372	1375
		1372	1371
		1374
Mean,		1373	1372	1370	1370
					1370

Point 6 is the quintuple point for $\text{MgO} \cdot \text{Al}_2\text{O}_3$, $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ and Al_2O_3 (CaO 21, Al_2O_3 74, MgO 5). Its melting temperature determined in the iridium furnace is $1680^\circ \pm 20^\circ$.

Point 6 was located by extrapolation of the boundary curves 5-6, H-6 and C-6.

The Concentration-Temperature Model.

In the preceding pages we have recorded equilibrium temperatures as determined within the limits of our apparatus for the three binary systems and for the ternary system; in other words, we have presented the temperature corresponding to quintuple points, boundary curves and fields. By interpolation from the determined melting temperatures we may draw constant temperature lines or isotherms; this has been done for every 100° from 1400° to 1600° and the resulting diagram is given in Fig. 5, which shows, moreover, the melting temperatures of each compound, component, quadruple and quintuple point.

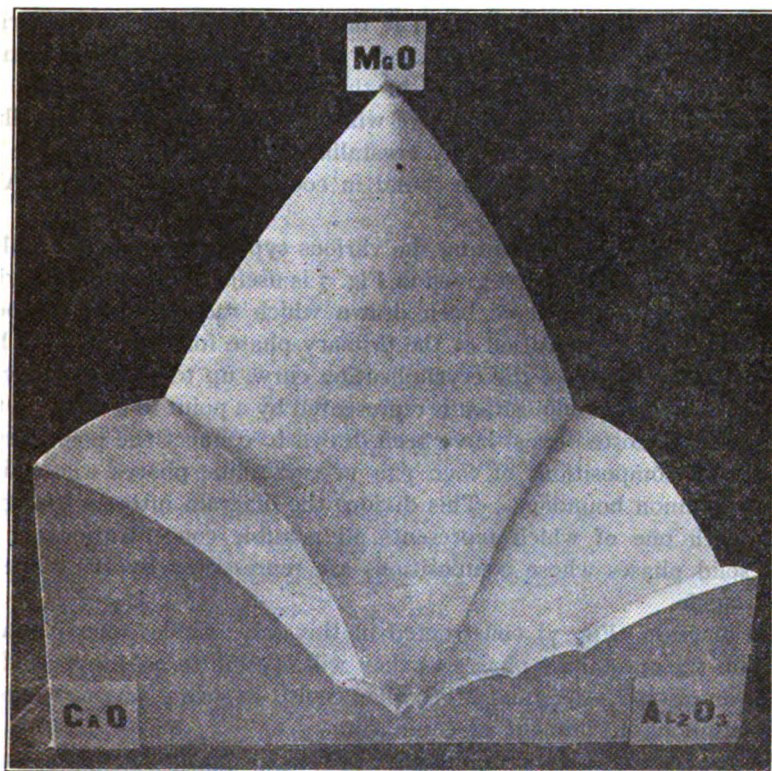


Fig. 6.—Photograph of solid model of concentration-temperature diagram of the system $\text{CaO-Al}_2\text{O}_3\text{-MgO}$.

By erecting the diagram (Fig. 4) for each boundary curve (Fig. 3) perpendicular to the plane of the corresponding projection of each boundary curve (Fig. 3) one can construct a concentration-temperature solid model whose surface represents the melting temperatures of all ternary compositions of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$. A photograph of a solid plaster of Paris model constructed in this way is given in Fig. 6. Fig. 6 is taken from in front of the $\text{CaO-Al}_2\text{O}_3$ side and shows the slopes of the various fields.

Crystallization of Ternary Solutions of $\text{CaO-Al}_2\text{O}_3\text{-MgO}$.

The results of this investigation thus far, have been plotted graphically in diagrams to show the equilibria between the various phases of this system $\text{CaO-Al}_2\text{O}_3\text{-MgO}$. To the end that these data be utilized in practical work it is desirable to know what is the composition of the solid phases which separate when any ternary solution is cooled. In the previous paper the systematic elaboration of phase separations has been carried out, the deductions being based on the actual data contained in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$. The data contained in the equilibrium diagram for the present system shows that the same types of ternary crystallization are found here as in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$. For that reason in the present paper we will treat the subject of crystallization rather briefly, giving merely crystallization curves, to illustrate the various types of crystallization found in cooled solutions of CaO , Al_2O_3 and MgO .

For the purpose of illustrating the various types of ternary crystallization, a diagram such as that given in Fig. 7 is useful. In this equilibrium diagram, straight lines have been drawn which radiate from the point representing the composition of the primary phase for each field. These lines show the course of the crystallization curve up to the boundary for any solution whose composition is represented by a point in a field. Other straight lines (dotted lines) have been drawn to connect the points representing the compositions of each pair of crystalline phases whose fields have a common boundary. This divides the diagram into six triangular areas, each one of which represents all possible concentrations of the three solid phases whose compositions are represented by the apices of the triangle.

The diagram (Fig. 7) constructed in this way enables one to readily ascertain the crystalline phases as they will crystallize or disappear from a solution of CaO , Al_2O_3 and MgO when cooled in such a way as to secure the continuous attainment of equilibrium.

The experimental data represented in this diagram show that there are five types of ternary crystallization found therein. Each of these types involves only crystalline phases of constant composition, that is, there is no solid solution. These five types are: (1) Crystallization in

which the crystallization of each solid phase is continuous. (2) Crystallization in which a solid having crystallized along a boundary partially disappears at a quintuple point. (3) Crystallization in which a solid having crystallized along a boundary entirely disappears at a quintuple point.

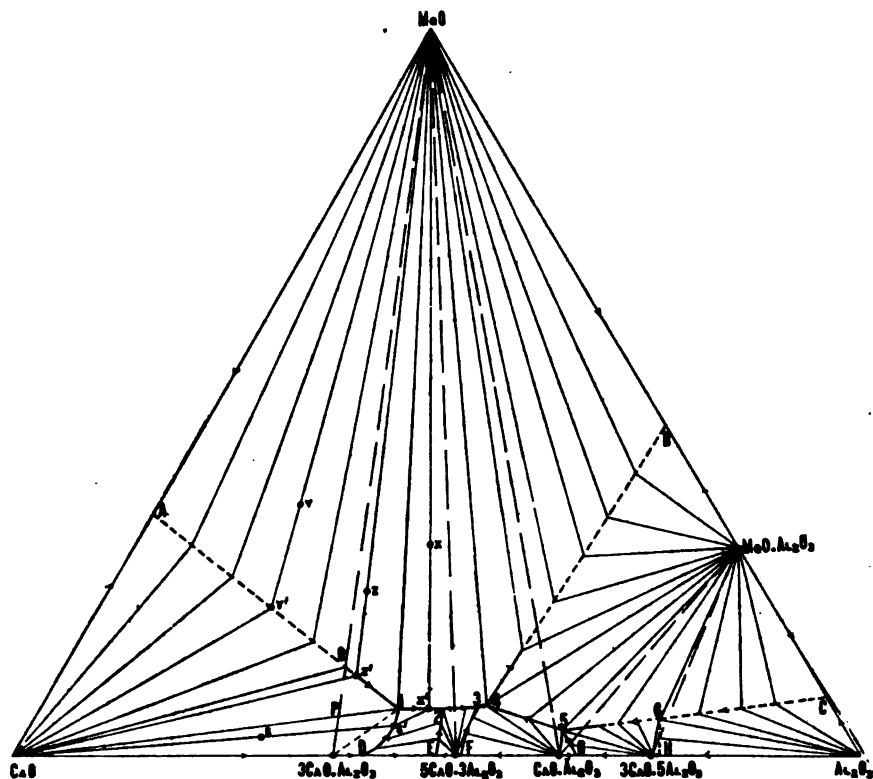


Fig. 7.—Equilibrium diagram to show the course of crystallization when ternary solutions of CaO , Al_2O_3 , MgO are cooled.

point. (4) Crystallization in which a solid phase having crystallized within a field partially disappears along a boundary curve. (5) Crystallization in which a solid phase having crystallized within a field entirely disappears along a boundary.

We will now consider each of these five types separately, giving the course of the crystallization curve for a single particular solution and the areas which represent the compositions of all solutions which on cooling show the same type of ternary crystallization.

1. Crystallization in which the Crystallization of Each Solid Phase is Continuous.—The crystallization curve follows a straight line to a boundary, along which two phases crystallize until the quintuple point (a eutectic) is reached when three phases crystallize and the solution

completely solidifies. As an example consider a saturated solution whose composition is represented by point X. The course of its crystallization curve is from X to X' and from X' to 2. The solid phases in the order in which they crystallize are pure MgO; MgO and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ together; and finally MgO, 3CaO , Al_2O_3 and $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$. Examination of Fig. 7 shows that there are 4 areas which represent the compositions of solutions which on cooling have this type of crystallization, *viz.*, D-1-2-E; E-2-3-F; F-3-4- $\text{CaO} \cdot \text{Al}_2\text{O}_3$; 1-MgO-4-3-2.

2. Crystallization in which a Solid having Crystallized Along a Boundary Partially Disappears at a Quintuple Point.—The crystallization curve follows a straight line to a boundary along which two phases crystallize until a quintuple point (not a eutectic) is reached. At the quintuple point one of the two phases which has crystallized partially disappears—unites with a component in solution to form the third crystalline phase. As an example consider the crystallization curve for solution γ . Its course is from γ to γ' and from γ' to 1 where it ends. The solid phases in the order in which they appear are MgO; MgO and CaO together; and finally MgO, CaO and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. Part of the CaO which crystallized with MgO unites with Al_2O_3 in solution to form $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. There are 4 areas which represent the compositions of solutions which on cooling show this type of ternary crystallization, *viz.*, CaO-A-MgO-P; MgO-B-MgO $\cdot \text{Al}_2\text{O}_3$ - $5\text{CaO} \cdot \text{Al}_2\text{O}_3$; $\text{CaO} \cdot \text{Al}_2\text{O}_3$ -MgO $\cdot \text{Al}_2\text{O}_3$ - $6-3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$; Al_2O_3 -MgO $\cdot \text{Al}_2\text{O}_3$ - $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$.

3. Crystallization in which a Solid having Crystallized Along a Boundary Entirely Disappears at a Quintuple Point.—The crystallization curve follows the same course as in (2) up to the quintuple point. At this point one phase which has crystallized along a boundary is entirely used up in the formation of the third solid phase. The crystallization curve now leaves the quintuple point and follows a boundary along which the two remaining solid phases continue to crystallize until a second quintuple point is reached which is the end of the curve. As an example consider the crystallization for a solution whose composition is represented by point z within the field of MgO. Its course is from z to z' , from z' to 1 and from 1 to 2, where it ends. The solid phases in the order in which they appear are: MgO; MgO and CaO; MgO, CaO and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$; CaO and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$; and finally MgO, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$. All of the CaO which crystallized united with Al_2O_3 in solution to form $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. There are 4 areas which represent the compositions of solutions which on cooling show this type of ternary crystallization, *viz.*, o-MgO-1-P; 3MgO -CaO $\cdot \text{Al}_2\text{O}_3$; CaO $\cdot \text{Al}_2\text{O}_3$ - $5\text{MgO} \cdot \text{Al}_2\text{O}_3$; $6\text{MgO} \cdot \text{Al}_2\text{O}_3$ - $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$.

4. Crystallization in which a Solid having Crystallized Within a Field Partially Disappears Along a Boundary.—The crystallization curve follows a straight line to a boundary, one phase crystallizing until the

boundary is reached when part of the primary phase is used up in the formation of a second solid phase. Proceeding in this way, one phase disappearing while the other crystallizes, the crystallization curve follows a boundary to a quintuple point. As an example consider Solution S within the field of CaO . The course of its crystallization curve is from S to S' and from S' to 1, where it ends. The solid phases in the order in which they appear are: CaO ; CaO and $3\text{CaO}.\text{Al}_2\text{O}_3$; and finally CaO , $3\text{CaO}.\text{Al}_2\text{O}_3$ and MgO . The CaO which crystallized as primary phase unites with Al_2O_3 in solution to form the secondary phase $3\text{CaO}.\text{Al}_2\text{O}_3$. There are two areas which represent the compositions of solutions which on cooling show this type of ternary crystallization, *vis.*, $\text{CaO}-\text{P}-3\text{CaO}.\text{Al}_2\text{O}_3$; and $\text{P}-1-3\text{CaO}.\text{Al}_2\text{O}_3$. Crystallization curves for area $\text{CaO}-\text{P}-3\text{CaO}.\text{Al}_2\text{O}_3$ will end at 1 while those for area $\text{P}-1-3\text{CaO}.\text{Al}_2\text{O}_3$ will end at quintuple point 2, since this area is included within the triangle which represents all possible concentrations of $3\text{CaO}.\text{Al}_2\text{O}_3$, MgO and $5\text{CaO}.\text{Al}_2\text{O}_3$ whose quintuple point is point 2.

5. Crystallization in which a Solid Phase having Crystallized Within a Field Entirely Disappears Along a Boundary Curve.—The crystallization curve follows a straight line to a boundary along which the primary phase is entirely used up in the formation of the secondary phase. The curve now leaves the boundary and crosses a field, a single solid crystallizing until a second boundary is reached when two phases crystallize and the curve proceeds along the boundary to a quintuple point, where it ends. As an example consider any solution whose composition is represented by a point within area $\text{D}-1-3\text{CaO}.\text{Al}_2\text{O}_3$. The crystallization curve for any such solution will intercept boundary $\text{D}-1$, leaving boundary $\text{D}-1$ and cross the field $\text{D}-1-2-\text{F}$, intercept either boundary $1-2$ or $\text{E}-2$ and end at 2. The solid phases in the order in which they appear are: CaO ; CaO and $3\text{CaO}.\text{Al}_2\text{O}_3$; $3\text{CaO}.\text{Al}_2\text{O}_3$; $3\text{CaO}.\text{Al}_2\text{O}_3$ and MgO if the curve intercepts boundary $1-2$ and $3\text{CaO}.\text{Al}_2\text{O}_3$ and $5\text{CaO}.\text{Al}_2\text{O}_3$ if it intercepts boundary $\text{E}-2$; and finally MgO , $3\text{CaO}.\text{Al}_2\text{O}_3$ and $5\text{CaO}.\text{Al}_2\text{O}_3$. There is but one area which represents the compositions of solutions which on cooling show this type of ternary crystallization, *vis.*: $\text{D}-1-3\text{CaO}.\text{Al}_2\text{O}_3$.

We have now given an example of each type of ternary crystallization and the areas which represent the compositions of solutions which on cooling give the same type. Knowing, then, the original composition of a ternary solution of CaO , Al_2O_3 and MgO , one can ascertain from the equilibrium diagram precisely which phases separate, their order of crystallization and the final product of crystallization.

The final product of crystallization of ternary solutions of CaO , Al_2O_3 and MgO always consists of three solid phases whose fields are adjacent. The same three solid phases will be the final product of crystallization

from any solution whose composition lies within the triangle formed by lines joining the compositions of these three phases.

These composition lines which have been drawn in Fig. 7 divide the diagram into 6 triangular areas. Each of these triangles represents all possible mixtures of those three compounds whose compositions are represented by the apices of the triangle. Though three certain, definite compounds can exist together in only one triangle, yet, as can be seen in the diagram, any one of these three compounds may be in a number of different triangles.

Summary.

The foregoing pages are a record of an investigation of the system $\text{CaO-Al}_2\text{O}_3\text{-MgO}$. This ternary system proved to be rather a simple one, there being no ternary compounds stable in contact with melt. The working out of this system, therefore, simply involved the equilibrium of the components (CaO , Al_2O_3 , MgO) and the binary compounds ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, $\text{CaO} \cdot \text{Al}_2\text{O}_3$, $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$, $\text{MgO} \cdot \text{Al}_2\text{O}_3$) in ternary solutions.

The relations found to subsist between the components and compounds in binary systems and in the ternary system are exhibited in a series of concentration-temperature diagrams.

The optical and crystallographical properties of the components and pure compounds are given in the previous papers, but a few additional notes are made here on the compounds $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and $\text{CaO} \cdot \text{Al}_2\text{O}_3$. A new form of Al_2O_3 has been described. The relation of this new form ($\beta\text{-Al}_2\text{O}_3$) to $\alpha\text{-Al}_2\text{O}_3$ (corundum), the only form previously observed, could not be definitely established, although it would appear that $\beta\text{-Al}_2\text{O}_3$ is monotropic with respect to $\alpha\text{-Al}_2\text{O}_3$. The relation of each of these forms, in the binary system $\text{MgO-Al}_2\text{O}_3$, involved solid solution, the extent of which was determined.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

THE EFFECT OF FREEZING ON CERTAIN INORGANIC HYDROGELS.¹

BY H. W. FOOTE AND BLAIR SAXTON.

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The composition and nature of precipitated colloids or hydrogels, such as silicic acid and ferric hydroxide, have been the subjects of repeated investigations which have varied greatly in their results. In the earlier work, the composition of inorganic hydrogels was determined chiefly

¹ Part of a dissertation presented by Blair Saxton to the Faculty of the Graduate School of Yale University, 1915, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

by drying the precipitates under fixed empirical conditions, and the results obtained were nearly as variable as the conditions of experiment. Later investigators have used other methods, of which the following are the chief: A dynamic method which consists in measuring the velocity of dehydration at constant temperature, which was used by Ramsay¹ and later by Tschermak;² a method depending on dehydration at gradually increased temperature, which was used by Carnelley and Walker,³ and by Baikow;⁴ a static method which consists in determining the vapor pressures during the course of dehydration, which was used by Van Bemmelen⁵ and later by Zsigmondy and his co-workers;⁶ a method devised by one of us⁷ which consists in determining the composition of the hydrogel at the point where its vapor pressure falls below that of pure water; and lastly a thermal method used by Müller-Thurgau⁸ and by Fischer⁹ and his co-workers, in which the heat effect caused by the freezing of water in the hydrogels was measured. From that value, the amount of water frozen was calculated. This method has not been applied to inorganic colloids so far as we are aware.

Nearly all the methods of investigation have been based, directly or indirectly, on the vapor pressure exerted by the hydrogels, but it has been difficult to draw definite conclusions as to the condition of the water in hydrogels from a knowledge of the vapor pressure alone. This is due to the fact that water, no matter what its condition, always exerts a vapor pressure and any change in the condition of the water must be judged by changes in direction of the vapor-pressure curve or of curves derived from it, rather than from any absolute values. The work of Van Bemmelen and, in particular, of Zsigmondy and his co-workers,¹⁰ has made it extremely probable that the water which evaporates from the hydrogel of silicic acid immediately after free water has been removed, and at a vapor pressure below that of pure water, is capillary in character, while the last of the water, coming off at the lower pressures, is combined or perhaps in solid solution.

In the present article, we shall give the results thus far obtained with

¹ *J. Chem. Soc.*, 32, 395 (1877).

² *Z. physik. Chem.*, 53, 349 (1905); *Z. anorg. Chem.*, 63, 230 (1909); *Monatsh.*, 33, 1151 (1912).

³ *J. Chem. Soc.*, 53, 59 (1888).

⁴ *Kolloid. Zeit.*, 2, 374 (1907).

⁵ *Z. anorg. Chem.*, 5, 467 (1893); 13, 233 (1897); 20, 185 (1899).

⁶ Zsigmondy, Bachman and Stevenson, *Ibid.*, 75, 189 (1912); Bachman, *Ibid.*, 79, 202 (1913); Anderson, *Z. physik. Chem.*, 88, 191 (1914).

⁷ *THIS JOURNAL*, 30, 1388 (1908).

⁸ See Fischer, *Beitr. Biol. Pflanz.*, 10, 200, 232 (1911).

⁹ *Biochem. Z.*, 18, 58 (1909); 20, 143 (1909); *Beitr. Biol. Pflanz.*, 10, 133 (1911); *Kolloid. Zeit.*, 8, 291 (1911).

¹⁰ *Loc. cit.*; also *Z. anorg. Chem.*, 71, 356 (1911); 73, 158 (1911).

several inorganic hydrogels in an attempt to determine the water which can be separated from them by freezing. This is a determination of considerable interest, for it is to be expected that water which is present as a liquid can be converted into ice if the temperature is sufficiently lowered, even when the water is present in minute capillaries, while water which is combined as a solid hydrate cannot in general be separated by this means. A determination of the ice which can be produced in a hydrogel should therefore give a means of judging between capillary and combined water in a way which has not before been possible.

Since the method used in the present investigation is based on freezing the uncombined water in the hydrogels, we shall first consider previous observations on the effect of freezing on these precipitates. The earliest experiments on this subject are those of Limberger,¹ Wittstein² and Leroy,³ all of whom stated that they obtained crystalline ferric hydroxide by freezing the amorphous precipitate. Van Bemmelen and Klobbie⁴ repeated this experiment and showed that no crystalline hydrate was obtained. They found that freezing had little effect except to remove included water. Ruff⁵ found that ferric hydroxide before and after freezing at -10° and -185° had the same composition, $\text{Fe}_2\text{O}_3 : 4.2\text{H}_2\text{O}$, when dried over 15% sodium hydroxide. The first important contribution is that of Lottermoser.⁶ He froze silicic acid which appeared dry and found that water separated, leaving silicic acid as a granular mass. He explained this by assuming that water in the capillaries had expanded on freezing and broken the fine porous structure. It is interesting to note that he suggested freezing as a means of drying gelatinous precipitates of the silica type. Bruni⁷ froze silicic acid and analyzed the residue, concluding that it has no constant composition. It should be pointed out, however, that it is very difficult to separate water, after melting, from the residue and constant results could hardly be expected. The heat evolved when water is frozen from a colloid has been used in calculating the amount of uncombined water in the substance. This method has been used by Müller-Thurgau and by Fischer.⁸ The former measured the heat evolved directly while Fischer calculated it from the velocity of cooling. Their work was with organic hydrogels. A very complete bibliography on the effect of freezing on colloids, organized, organic and inorganic, may be found in Fischer's articles.

¹ *Jahresb.*, 1853, 370.

² *Ibid.*, 1853, 370.

³ *Ibid.*, 1854, 363.

⁴ *J. prakt. Chem.*, [2] 46, 497 (1892).

⁵ *Ber.*, 34, 3417 (1901).

⁶ *Ibid.*, 41, 3976 (1908).

⁷ *Ibid.*, 42, 563 (1909).

⁸ *Loc. cit.*

Method.

The method which we have used consists in freezing the precipitate, of known total water content, in a dilatometer and measuring the expansion caused by freezing the uncombined water. From the expansion, the amount frozen may be calculated and the amount of combined water obtained by difference.

The dilatometer had the usual form. The stem was calibrated by means of mercury. Ligroin was used to fill the bulb and mark changes in volume. It has the advantage of high vapor pressure, making it possible to fill the bulb completely by the use of an ordinary water pump. For temperatures as low as -20° , an ice-salt bath was used. For still lower temperatures, a mixture containing about equal weights of ice and calcium chloride was necessary. This mixture must be well protected against radiation. A convenient holder for our purpose consisted of a quart wide-mouthed thermos jar. In practice, the temperature of the dilatometer was lowered gradually in the ice-salt bath to about -20° and then directly to about -30° in the other. It was not practicable to lower the temperature gradually between -20° and -30° . The temperature could, however, be raised gradually from -30° by the cautious addition of water.

In carrying out a determination, the dilatometer readings at first show a regular decrease, as the temperature falls, due merely to contraction of the bulb and contents. At a temperature usually several degrees below zero, sudden expansion occurs, due to freezing. The water freezing in this first expansion consists of free water and that part of the capillary water whose freezing point has been reached. After the volume has become constant, a further lowering of temperature causes more capillary water to freeze and the volume usually expands somewhat farther, after which, contraction sets in, and, if the temperature is sufficiently lowered, the contraction finally becomes very nearly a linear function of the temperature, as it is before freezing occurs. On raising the temperature, the expansion is nearly linear for some distance but at a temperature still below 0° contraction sets in, due to melting, and the volume finally returns to its original value above 0° .

The following diagram (Fig. 1) illustrates the typical behavior. Dilatometer readings or volumes are plotted as ordinates and temperatures as abscissas. The line AB shows the normal contraction before freezing, BC the sudden expansion when freezing begins, CD the expansion and contraction on further cooling and DF the expansion and contraction as the temperature is raised. DE is the linear extension of the heating curve from D. Beginning at D the curve DF was found to be a straight line for a considerable distance, showing that capillary water, when once frozen, does not melt at as low a temperature as it freezes. The curve

downward near F shows there is a decided tendency to melt at a temperature still somewhat below 0° . The extrapolated line DE gives the normal expansion if no melting occurred and the length of a vertical line between AB and DE gives the expansion due to freezing all free and capillary water. As AB and DE are very nearly, but not quite, parallel, we have chosen the length of the vertical at -6° as a measure of the expansion. Its length has been determined graphically from the plotted values. To convert the expansion due to ice formation, expressed in cubic centimeters, into the corresponding weight, we have used Bunsen's data that 1 g. of water at 0° expands 0.09070 cc. on freezing. In this way, the total weight of water which is frozen can be determined.

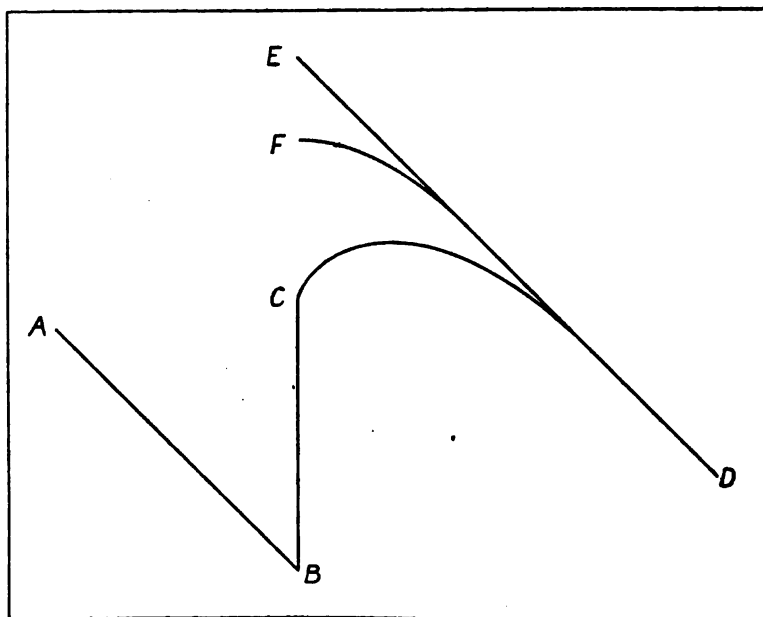


Fig. 1 (Diagrammatic).

It is not possible, from our results, to distinguish sharply between true capillary and free water, for the reason that supercooling always occurs in the dilatometer. If freezing occurred at 0° , the length of the vertical BC, measured at 0° , would give the free water, and of CE, the capillary. Where freezing occurs, as it does, several degrees below zero, the water freezing at this temperature is free water plus that capillary water whose freezing point has been reached. The length of BC therefore corresponds to free water and a part of the capillary water. It is possible, however, to determine with sufficient accuracy the capillary water separating below a certain temperature. We have chosen to determine the amount

separating below -6° and shall call this the *apparent capillary water*. The actual capillary water is always greater in amount.

The chief uncertainty in the method appears to be whether, at D, all capillary water has frozen. This point will be discussed under "combined water in the hydrogel of alumina."

Preliminary Determinations.

We shall give first the results of several preliminary determinations in the dilatometer, which were carried out with such materials that we could draw conclusions in advance as to the nature of the water present—whether free, capillary, or combined. A mixture of sand and water was used to show the behavior of free water. The behavior of free and capillary water was illustrated with moist lampblack, while moist calcium hydroxide furnished an illustration of free and combined water. It was of course necessary to choose materials which were not soluble to any extent in water. Otherwise, there would be a lowering of freezing point due to dissolved substances as well as to capillarity, an unnecessary complication which we wished to avoid.

The mixture of sand and water in the dilatometer behaved as expected. In this case there was no question of capillary or combined water and the experiment was carried out chiefly to show how closely free water could be determined. Freezing occurred at -4° and all water froze sharply at this temperature. The contraction before and after freezing was entirely regular and dilatometer readings on falling and rising temperatures were practically identical. The observations are plotted in Fig. 2. In

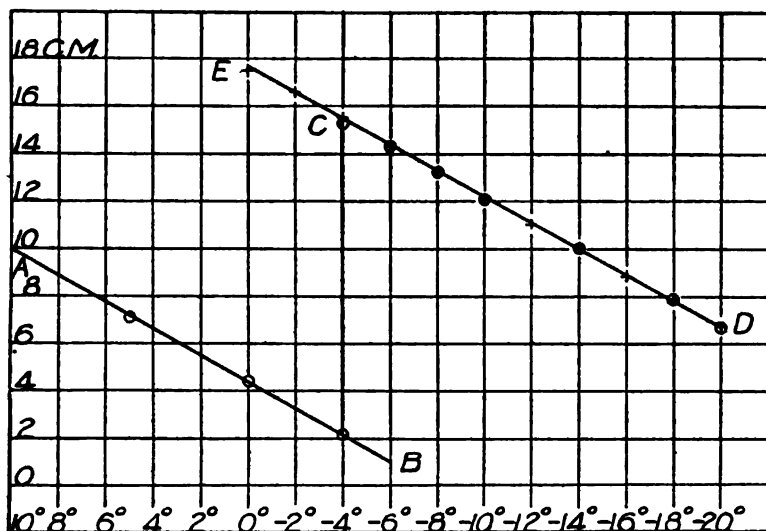


Fig. 2.—Sand and water.

this figure, as in all following, the corrected readings of the dilatometer in centimeters are plotted as ordinates; observations taken on falling temperature are represented by circles, and on rising temperature, by crosses. Necessary data and the result calculated from the observations are in the following table. The second column of the table gives the increase in volume due to freezing, measured in centimeters on the stem of the dilatometer. The third gives the corrected volume of 1 cm. of the dilatometer stem, expressed in cubic centimeters. The product gives the increase in volume due to ice formation, from which the weight of water found has been calculated.

SAND AND WATER.

Water taken, (g.).	Expansion due to freezing, (cm.).	Volume of 1 cm., (cc.).	Water found, (g.).	Error.
1.404	13.3	0.009751	1.430	0.026

Lampblack was used in the next experiment. It had previously been intensely ignited. A weighed amount was moistened with water and allowed to stand for two days. The material was then nearly dry to the touch but contained over 40% of water. This material, when introduced into the dilatometer, required a temperature of -28° to complete the freezing. Its behavior was thus entirely different from that of sand and

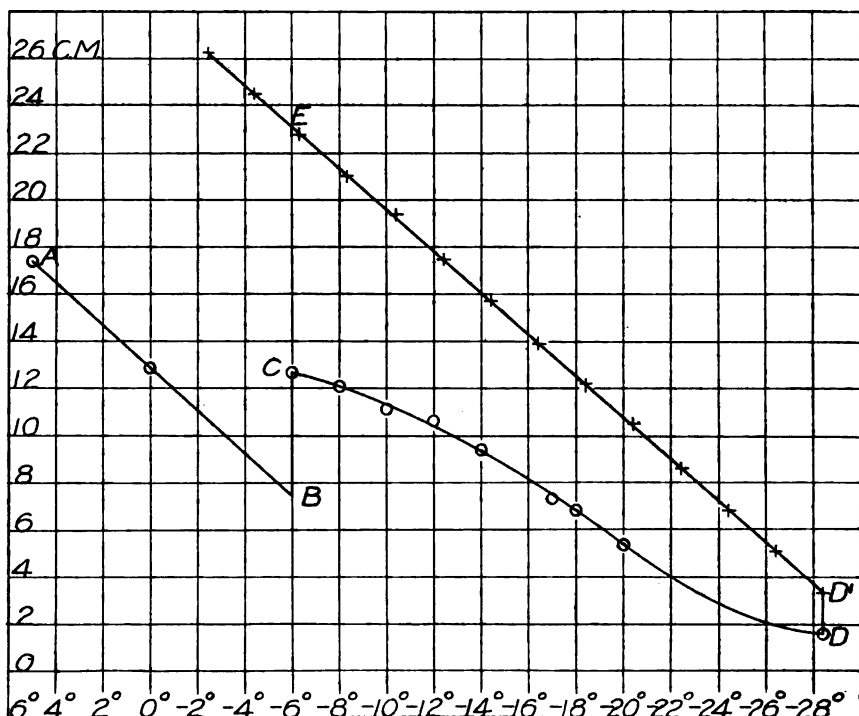


Fig. 3.—Lampblack and water.

water, due to the adsorbed or capillary water present. The observations are plotted in Fig. 3. Ice formed very slowly at the lower temperatures and when equilibrium had apparently set in at -28° , a further increase in volume occurred after two hours. This increase is represented in the figure by DD'. The results obtained are as follows:

LAMPBLACK AND WATER.

Lamp-black taken, (g.).	Water taken, (g.).	Total expansion due to freezing, (cm.).	Expansion due to freezing apparent capillary water, (cm.).	Volume of 1 cm., (cc.).	Total water found, (g.).	Apparent capillary water found.	Error in total water, (g.).
2.530	1.834	15.7	10.35	0.01058	1.831	1.207	0.003

The result for apparent capillary water shows that lampblack adsorbed water equal to nearly half its own weight in such a manner that a temperature much below 0° was necessary to freeze it. A part of the water in the hydrogels which we have investigated is strikingly similar in its behavior to this adsorbed or capillary water of lampblack.

It seemed possible that filter paper might take up water as lampblack does and it was tested in the same manner. The water in this case, however, froze almost as sharply as in the mixture of sand and water, only a very small amount freezing gradually at a lower temperature. The results need not be given here. The total water found agreed closely with the amount taken.

For the mixture of calcium hydroxide and water, pure calcium oxide, prepared from the carbonate, was introduced into the dilatometer and warm, moist air, free from carbon dioxide, was passed over the oxide till the increase in weight showed a considerable excess of water over that required to convert the lime into calcium hydroxide. The freezing curve was determined as usual. The observations are plotted in Fig. 4. The results obtained are as follows:

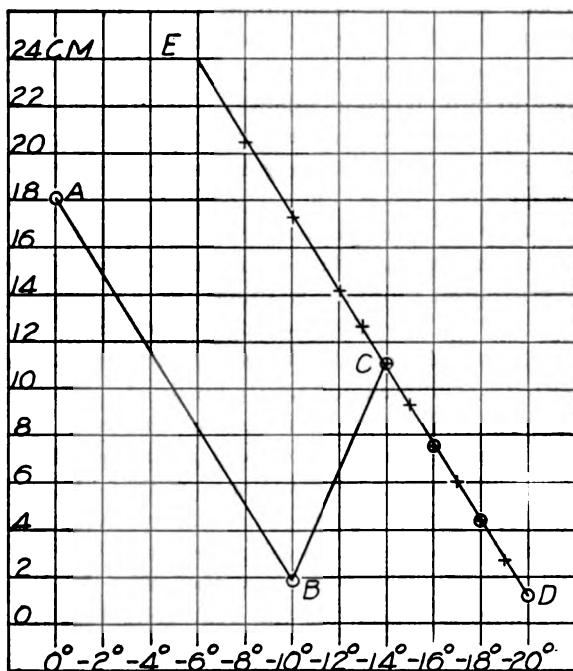


Fig. 4.—Calcium hydroxide and water.

CALCIUM OXIDE AND WATER.

CaO taken, (g.).	Total water taken, (g.).	Free and capillary water taken.	Expansion due to freezing, (cm.).	Volume of 1 cm.	Free and and capillary water found, (g.).	Error in free and capillary water.
3.921	2.510	1.251	16.0	0.006205	1.094	0.157

The amount of free water found is somewhat below the amount taken. The curve shows very well, however, the behavior of a hydrate containing very little capillary water, the curve CD being nearly a straight line and coinciding closely with DF.

The Hydrogel of Alumina.

In the dilatometer work on all the hydrogels, we have had two objects in mind: (1) to determine the general structure of the gels and how this varies with conditions; and (2) to determine, at least approximately, the amount of water which does not freeze and is therefore neither free nor capillary.

The hydrogel of alumina was the first with which we worked and many of the determinations were carried out using a minimum temperature of only -20° . These results serve to show the structure of the hydrogels and how it changes on freezing. It is probable, however, that not all the capillary water is removed at this temperature, so that the results on combined water in these determinations are undoubtedly high.

Four samples of aluminium hydroxide were prepared under varied conditions. It does not appear that the method of precipitation affects their character noticeably. All samples were washed free of chlorides. They were prepared as follows:

Sample A. Precipitated by ammonia from a cold dilute solution of the chloride. After washing, it was air-dried till it reached the composition desired.

Sample B. Precipitated by ammonia from a hot concentrated solution of aluminium chloride containing much ammonium chloride. It was air-dried after thorough washing.

Sample C. A part of Sample B before being dried in the air to any extent was thoroughly frozen. The granular residue remaining after melting was filtered and partly air-dried.

Sample D. Prepared like A but to hasten the drying it was frozen at a temperature a little below zero and remelted.

The dilatometer observations on these samples have been plotted in the curves which follow. The accompanying tables give other necessary data and also the results calculated from the observations.¹

The first experiments show the effect on capillary water of varying amounts of free water in the hydrogel. For this purpose, Sample A was air dried and two samples were taken during the drying, containing

¹ Tables of the values plotted in all figures are in the dissertation presented by Saxton.

decreasing percentages of water. The observations and results are shown in Figs. 5 and 6 and Table I.

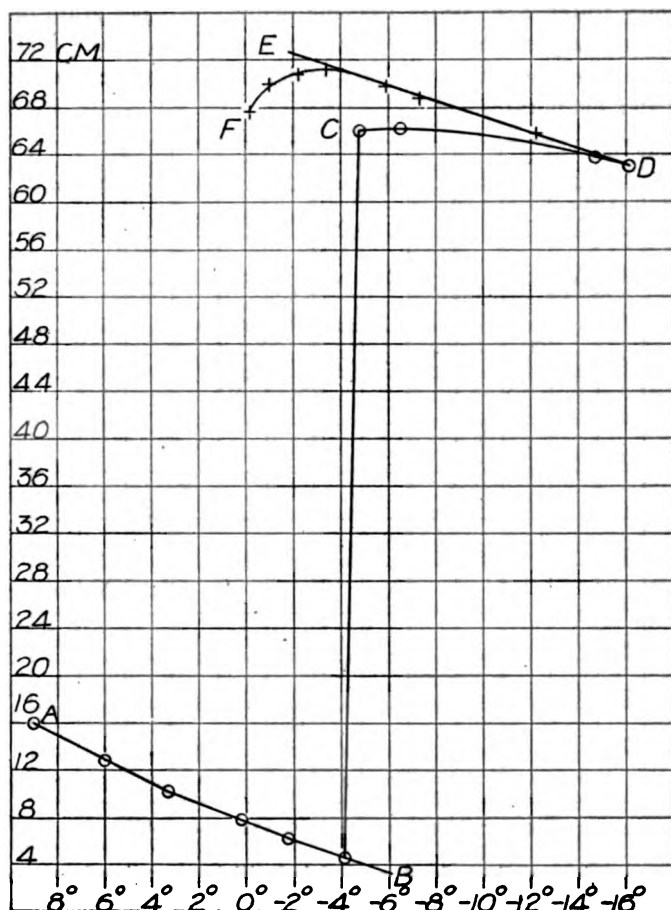


Fig. 5.—Alumina and water (75.2% water).

TABLE I.
Showing Effect of Water Content on the Capillary Water (Sample A).

No. of figure.	Wt. of hydrogel.	Per cent. H ₂ O in hydrogel.	Expansion due to apparent capillary water, (cm.).	Value of 1 cm. in cc.	Weight of apparent capillary water per g. Al ₂ O ₃ .
5	12.075	75.23	3.7	0.00920	0.1255
6	10.091	54.46	5.0	0.01058	0.1269

It is probable that the last of the capillary water was not frozen in either No. 5 or No. 6, but the results are comparable, as the lowest temperature in each case was about the same. Roughly, the difference between the

two results shows in the figures from the lengths of BC; that is, No. 5 contains much the larger proportion of free water. The amounts of apparent capillary water, *i. e.*, water freezing below -6° , per gram of alumina, are shown in the last column. The results are practically identical and indicate that the amount of capillary water in the sample does not change as free water evaporates.

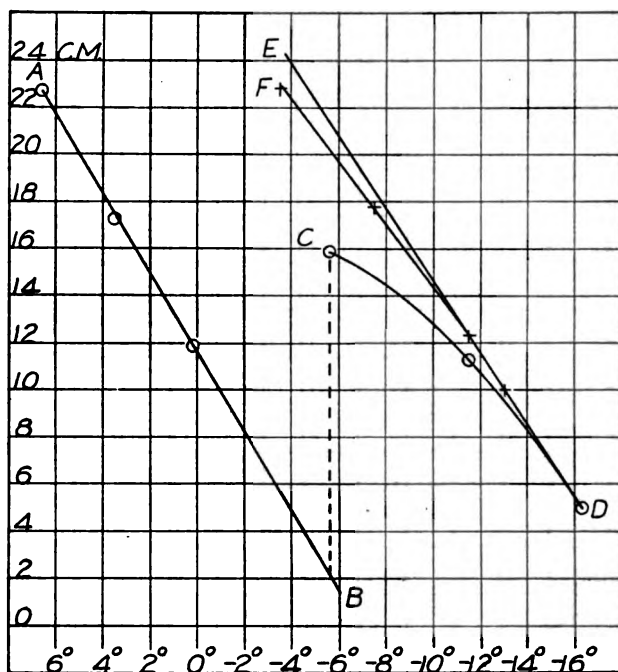


Fig. 6.—Alumina and water (54.46% water).

Another portion of Sample A was dried till it contained approximately the water content (38.18) corresponding to combined water alone. When cooled, the contraction in the dilatometer was entirely regular as far as the minimum temperature observed, -16.4° , and the dilatometer readings on falling and rising temperature lay on the same curve. Evidently, no water was frozen in this sample.

The change in appearance of alumina after freezing made it appear probable that the proportion of free water increased at the expense of capillary water by this process. To prove this, the same sample was frozen three times in the dilatometer. The observations on the first and the third freezing are plotted in Fig. 7. The contraction before freezing in both cases is represented by AB. The dotted lines show the results of the first freezing in this curve, as well as in all others where a precipitate has been frozen more than once. In order to avoid confusion

in the diagram, the observations on the second freezing are not plotted. The results obtained are in Table II.

TABLE II.

Determination of Free and Apparent Capillary Water, Showing Effect of Repeated Freezing.

Sample B. 58.09% H_2O . 8.655 g. substance. 1 cm. = 0.009751 cc.

No. of figure.	Treatment.	Expansion in cm. due to free and capillary water.	Wt. of free and capillary water.	Expansion in cm. due to apparent capillary water.	Wt. of apparent capillary water.	Wt. of apparent capillary water per g. Al_2O_3 .
7	Air dried	21.6	2.322	3.9	0.4192	0.1156
	Once frozen	22.1	2.376	1.5	0.1612	0.0445
7	Twice frozen	22.1	2.376	1.0	0.1075	0.0296

The results in the last two columns show that capillary water is reduced by each successive freezing. On the other hand, the table shows that the weight of free and capillary water, representing all the water frozen, changes but little in successive freezings. Stated in a somewhat different way, repeated freezing appears to convert most of the capillary water into free water, while there is but little effect on combined water.

The effect of freezing was also shown in another case. Sample B was thoroughly frozen, melted and partly air dried before placing it in the dilatometer. Two lots of this material (Sample C) were used in independent determinations. Both sets of observations are plotted in Fig. 8 and other data, with the results, are in Table III.

While the two curves are not identical, the capillary water is much less than in material which had not undergone previous freezing.

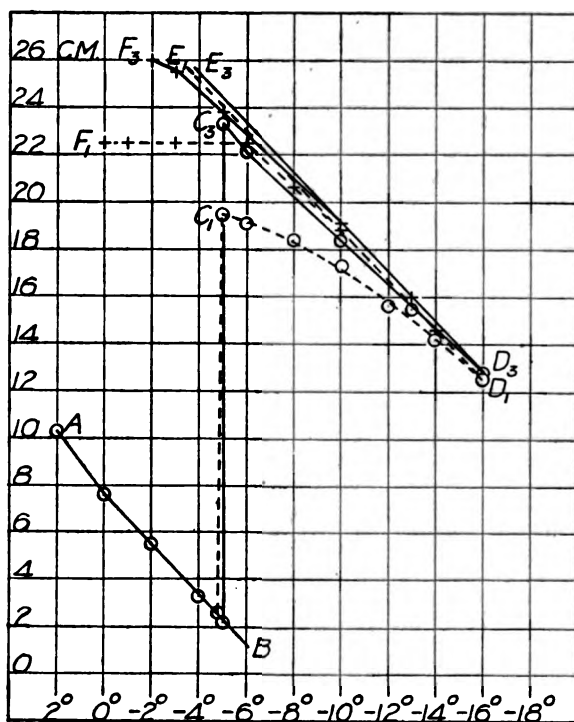


Fig. 7.—Alumina and water. (Effect of repeated freezing.)

TABLE III.
Determination of Apparent Capillary Water after Previous Freezing.
Sample C. 59.09% H₂O.

No. of figure.	Wt. of hydgel, (g.).	Expansion due to apparent capillary water, (cm.).	Volume of 1 cm., (cc.).	Wt. of apparent capillary water per g. Al ₂ O ₃ .
8a	4.401	0.05	0.009741	0.003
8b	5.996	1.4	0.009751	0.061

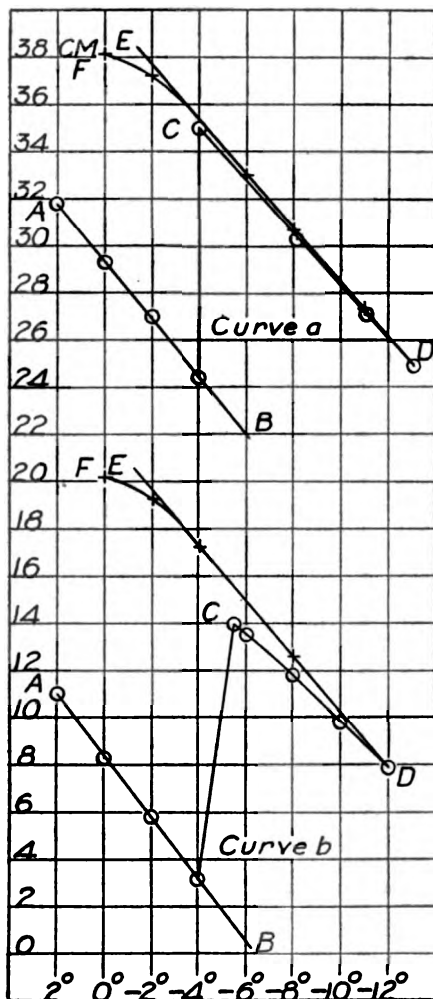


Fig. 8.—Alumina and water (material previously frozen).

lies well above D_1E_1 . In Fig. 7, on the other hand, where the material was fresh, D_1E_1 and D_2E_2 are close together, showing that total free and

The age of a hydgel appears to affect it considerably. Sample D has been used to show this. The sample was frozen first by placing it out of doors at a freezing temperature before it was sealed in the dilatometer. The material was granular after freezing but the temperature was not sufficiently low to affect the apparent capillary water as will be seen below. A temperature of -6° is required to affect this. The sample was then frozen in the dilatometer and the curve shown by the dotted lines in Fig. 9 was obtained. After standing eight months the sample was frozen again twice, once to -20° and again to approximately -32° . The curves for these two freezings coincided so nearly that only the last one is shown in the figure. A comparison of the curves in Fig. 9 with the ones in Fig. 7, where the material was frozen repeatedly soon after preparation, will show at a glance the difference in the two cases. The apparent capillary water diminished in both cases after each freezing, but in Fig. 9, the total free and capillary water, after long standing, is considerably greater than that found when the same precipitate was fresh, as D_2E_2

capillary water has changed but little after each freezing. It will be noticed too, in Fig. 9, that the water freezing at -6° after long standing, represented by the length of BC_3 , is greater than the total amount of free and capillary water freezing from the fresh material. There is evidently an appreciable amount of water in the fresh material which did not freeze

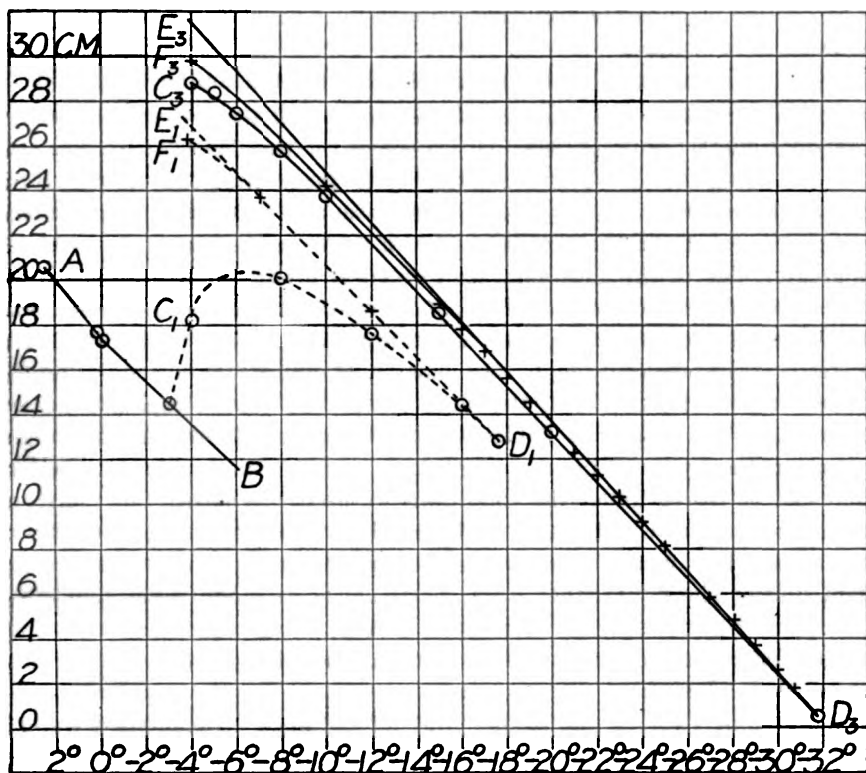


Fig. 9.—Alumina and water. (Effect of aging hydrogel.)

at -18° and would therefore be counted as combined water, which does, however, freeze without difficulty after long standing. We shall discuss this point below in considering combined water. The quantitative data regarding free and capillary water in this sample are in Table IV. The

TABLE IV.

Determination of Free and Capillary Water, Showing Effect of Age on the Hydrogel.

Sample D. 51.90% H_2O . 5.179 g. substance. 1 cm. = 0.006288 cc.

No. of figure.	Treatment.	Expansion due to free and capillary water, (cm.).	Wt. of free and capillary water, (g.).	Expansion due to apparent capillary water, (cm.).	Wt. of apparent capillary water.	Wt. of apparent capillary water per gram Al_2O_3 .
9	Fresh	13.6	0.9428	4.6	0.3189	0.1280
..	Stood 8 months	17.4	1.206	1.7	0.1179	0.0473
9	Stood 8 months	17.6	1.220	1.3	0.0901	0.0362

results show the character of the changes taking place, independent of whether all capillary water has been frozen or not.

The increase of free and capillary water is from 0.9428 g. to 1.220 g. while in Table II, the fresh sample, which was also frozen three times, showed but a slight increase in free and capillary water after each freezing. The change in apparent capillary water after each freezing is nearly the same in both samples.

Combined Water in the Hydrogel of Alumina.

An inspection of the diagrams for alumina will show that commonly the dilatometer readings near D are lower on the descending than on the ascending curve. This we interpret to mean that the temperature has not been sufficiently lowered in these cases and that freezing has taken place as far as D, so that on the curve for rising temperature, the volume is greater, due to the additional ice formed at lower temperatures. It is probable that in these cases, all capillary water has not been frozen even at D, and the results on capillary water are therefore low while combined water is correspondingly high. In general, of course, the lower the minimum temperature obtained, the more completely should capillary water be frozen. The results in Table IV and Fig. 9 have shown that a change occurs in the hydrogel on standing which increases the amount of water that can be frozen under the conditions we used. Whether this increase comes from water which was actually combined with alumina, or whether it was capillary water of too low a freezing point to appear earlier, our data do not show. Further work, particularly at much lower temperatures, will be necessary to decide this. It is, however, evident that the values for combined water in old material should represent equilibrium better than where fresh material was used.

We give in Table V the results thus far obtained on combined water. The necessary data have been taken from the previous tables and diagrams. The free and capillary water actually frozen in each determination is measured by the length of the vertical BE. As the total water is known, it is a simple matter to calculate the unfrozen. Where a sample has been frozen more than once, the results of the final freezing only are given in the table. The last column gives the percentage of unfrozen water

TABLE V.

No. of figure.	a. Wt. of hydrogel, (g.).	b. Wt. of Al_2O_3 , (g.).	c. Total H_2O , (g.).	d. Free and capillary H_2O , (g.).	e. Unfrozen H_2O , (g.).	Per cent. of H_2O unfrozen $\frac{100 e}{b + e}$.
5.....	12.075	2.991	9.084	6.755	2.329	43.8
6.....	10.091	4.595	5.496	2.251	3.245	41.4
7.....	8.655	3.627	5.028	2.376	2.652	42.2
8a.....	4.401	1.800	2.601	1.181	1.420	44.1
8b.....	5.996	2.453	3.543	1.537	2.006	45.0
9.....	5.179	2.491	2.688	1.220	1.468	37.1

remaining in the hydrogel, after deducting the water which has frozen. This is the same as the percentage of combined water in the hydrogel, if all capillary water is frozen.

The results vary considerably for reasons previously given. The last value, 37.1% of combined water, is undoubtedly the best. It was obtained on material which had been allowed to age for eight months and the lowest temperature of any was used in the freezing. There is the following evidence that all capillary water was frozen in this material. When frozen the first time after standing eight months, the temperature was lowered to only -20° . On the next freezing, the minimum temperature was nearly -32° . In spite of this difference of 12° , the line DE (Fig. 9) for the last freezing almost exactly covers the first (not shown in the diagram) which means that no additional ice formed below -20° in the last freezing. This is also shown by the fact that the curves CD and DF very nearly coincide for a considerable distance from D. It seems very probable therefore that all, or nearly all, free and capillary water was frozen in this sample and that the result, 37.1%, represents more closely than any of the others, the percentage of combined water in alumina. The calculated percentage of water in $\text{Al}(\text{OH})_3$ is 34.6, a value 2.5% below the result found.

We have the following additional evidence that the result obtained above is nearly correct: A sample of alumina was dried over sulfuric acid till it contained 33.9% H_2O . It was then rehydrated over water till it contained 39.4%. This material, in the dilatometer, separated a little ice between -5° and -8° . Below this, the cooling and heating curves were straight lines and coincided exactly, the temperature being lowered to -31.4° . Allowing for the ice which separated, the residue contained 37.5% H_2O , a value very close to that given previously for combined water. The fact that below -6° , the cooling and heating curves coincide so exactly, is very strong evidence indeed that all free and capillary water was frozen. It follows that all of the water up by the partly dehydrated alumina which did not freeze, amounting to 3.2%, must have been recombined. As will be shown below, the water taken up by partly dehydrated silica behaves quite differently.

The Hydrogel of Silica.

Silicic acid was prepared from a dilute solution of sodium silicate. One hundred and twenty grams of this salt were dissolved in four liters of water and the solution acidified with hydrochloric acid. Silica was precipitated from this solution by the addition of ammonia. It was partly washed by decantation and then treated with hydrochloric acid to remove any basic oxides. Finally it was washed till chlorides were removed. The precipitate was divided into two parts, one of which, SiO_2 (I), was frozen and melted before placing it in the dilatometer while the other,

SiO_2 (II), was dehydrated in a current of dry air at ordinary temperature till dry in appearance. In freezing and melting SiO_2 (I), a considerable quantity of water was removed, leaving it granular in appearance. This is identical with the behavior observed by Lottermoser.¹ The water thus frozen out contained only a trace of chlorides. A third sample was prepared, starting with a part of SiO_2 (II). The latter was dried over concentrated sulfuric acid at room temperature and then rehydrated over water till saturated. This sample is called SiO_2 (II-a).

Dilatometer observations were taken like those on alumina except that lower temperatures were commonly used. In Fig. 10, the curves of SiO_2 (I) are given for the first and third freezings in the dilatometer.

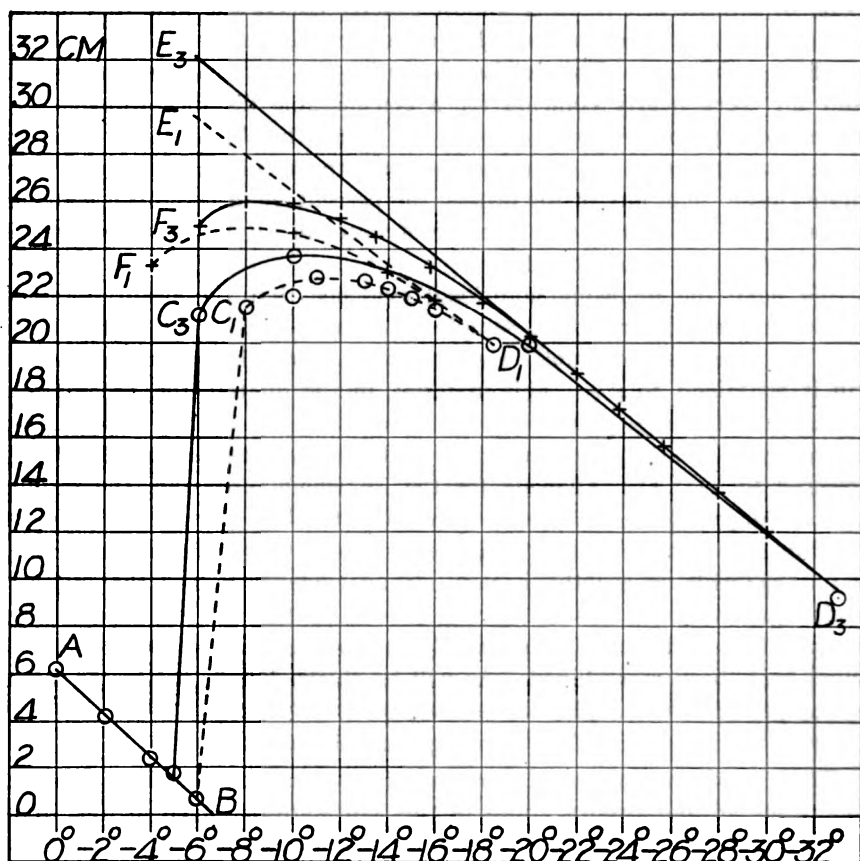


Fig. 10.—Silica and water (I).

The curve for the second freezing nearly coincides with that of the third and is not shown in the diagram. The minimum temperature on freezing

¹ Ber., 41, 3976 (1908).

the first time was not sufficiently low, as may be seen by inspecting the diagram, and only the results obtained from the second and third freezings are given (Table VI).

TABLE VI.

SiO₂ (I).—Results Obtained on Last Two Freezings.

71.18% H₂O. 6.131 g. hydrogel. 1 cm. = 0.01064 cc.

a. SiO ₂ in hydrogel, (g.).	b. Expansion due to free and capillary water, (cm.).	c. Free and capillary water, (g.).	d. Expansion due to apparent capillary water, (cm.).	e. Apparent capillary water per g. SiO ₂ , (g.).	f. Unfrozen water, (g.).	g. Per cent. of unfrozen water $\frac{100f}{a+f}$.
1.767	31.3	3.672	12.3	0.817	0.692	28.1
1.767	31.3	3.672	10.8	0.717	0.692	28.1

SiO₂ (II) was frozen twice in the dilatometer. Both curves were identical except that they differed slightly on the initial expansion when freezing began, and only the second is given in Fig. 11. Freezing began at so low

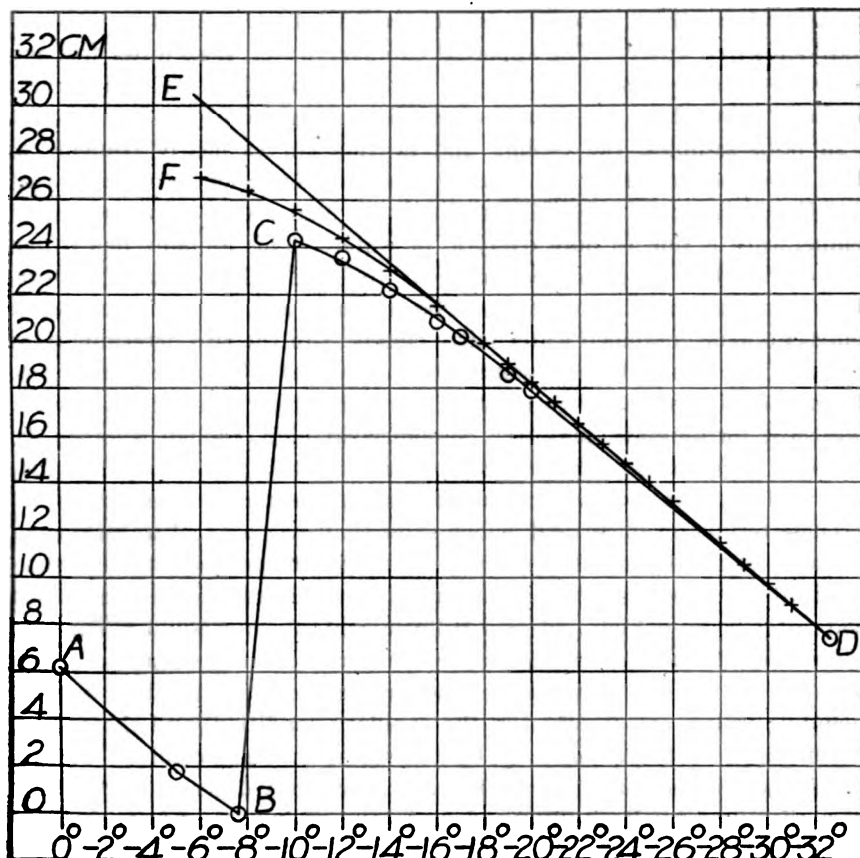


Fig. 11.—Silica and water (II).

a temperature that the result for apparent capillary water, by extrapolating to -6° has no value. The other results are given in Table VII.

TABLE VII.
 SiO_2 (II).—Identical Results Obtained on Both Freezings.
 78.36% H_2O . 4.903 g. hydrogel. 1 cm. = 0.01064 cc.

a.	b.	c.	d.	e.
SiO_2 in hydrogel, (g.).	Expansion due to free and capillary water, (cm.).	Free and capillary water, (g.).	Unfrozen water, (g.).	Per. cent of un- frozen water. $\frac{100d}{a+d}$
1.061	29.1	3.414	0.428	28.7

As may be seen from Fig. 10 and Table VI, the capillary water in silicic acid behaves quite differently from that in alumina. From Fig. 10, the lengths of BC and BC_2 are nearly equal, showing that the amounts of free and of capillary water have changed but little on successive freezings. It is evident, therefore, that silica reabsorbs capillary water after it has been frozen and melted, while we have shown previously that the amount of capillary water in alumina continually decreases on freezing and yields free water. The apparent capillary water, *i. e.*, water freezing below -6° , amounts to over 0.7 g. per gram of silica. This is nearly six times as much as any sample of alumina contained.

In both samples, the cooling and heating curves nearly coincide in their lower portion, near D, showing that very little ice forms as low as D. For instance, in SiO_2 (II), at -20° , the increase in volume on rising temperature is due to only 0.035 g. of water. This amount has frozen by lowering the temperature from -20° to -33° . It appears, therefore, that nearly all capillary water has been frozen and the unfrozen water represents true combined water fairly closely. In the two determinations given in the tables this amounts to 28.1 and 28.7%, corresponding to the empirical formulas $\text{SiO}_2 \cdot 1.31\text{H}_2\text{O}$ and $\text{SiO}_2 \cdot 1.35\text{H}_2\text{O}$. These results, like those for alumina, may well be somewhat high, though whether the unfrozen water forms a definite compound like H_2SiO_3 , or a solid solution, with a slight excess of water, must for the present remain unsettled.

These results on silicic acid, which show that over 25% of water remain unfrozen in the hydrogel, appear at first sight to contradict the results obtained by Bachmann¹ and Anderson,² who have shown that silicic acid, after being dehydrated over sulfuric acid, absorbs equal volumes of various liquids and that the liquids are not absorbed in any simple molecular proportion. This is very strong evidence indeed that all these liquids, including water, are absorbed in the capillary condition, and that water, for instance, on being taken up by the silica, does not combine with it. The silicic acid used in our work, however, is entirely different in character from that used by Bachmann and Anderson, as it has not been first de-

¹ *Z. anorg. Chem.*, 79, 202 (1913).

² *Z. physik. Chem.*, 88, 191 (1914).

hydrated over sulfuric acid. It is evident that if the reaction between silica and water is not reversible, water may be combined originally and after dehydrating, it will only be taken up mechanically.

We have carried out one dilatometer experiment on silica which had first been largely dehydrated over sulfuric acid and then allowed to become saturated with water. The behavior of this material on freezing is quite different from that of silica which has not been previously dehydrated. The material SiO_2 (II-a) was dried over concentrated sulfuric acid till nearly constant in weight. It then contained 9.2% of water. It was then allowed to stand over water at room temperature till saturated. It then contained 50.96% of water. This material was frozen and melted twice. Cooling and heating curves were both taken the first time, while on the second freezing, only the heating curve, starting at -33° , was taken.

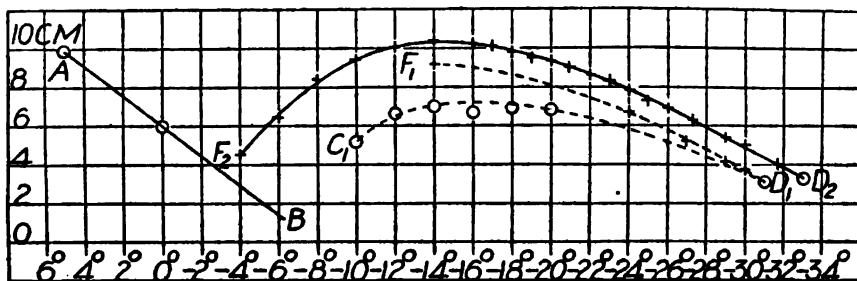


Fig. 12.—Silica and water. (Silica had previously been dehydrated.)

The observations are plotted in Fig. 12. The difference in character between these curves and those in Figs. 10 and 11, where the material had not been previously dehydrated, is quite striking. The curve C_1D_1 does not coincide with D_1F_1 in its lower part, showing that ice was still forming, as far as D_1 . Also, D_1F_1 and D_2F_2 begin to curve immediately on leaving D_1 and D_2 , showing that ice is melting at these extremely low temperatures. This is excellent evidence that water is present in much finer capillaries in this sample than in the others and supports the view that after dehydration, water reenters the silica in extremely fine capillaries. On account of the character of the curves, no quantitative data regarding capillary water can be derived from the diagram.

The Hydrogel of Ferric Oxide.

Ferric hydroxide was prepared by precipitating a solution of ferric chloride with ammonia. It was thoroughly washed by decantation and on the filter. Before use, it was frozen and melted. The water separated by this means was removed by filtering and the residue left exposed to the air till it appeared nearly dry. The sample was frozen twice in the dilatometer. Both series of observations are plotted in Fig. 13. The curves resemble somewhat those for alumina and silica and the presence

of the three kinds of water in the precipitate can readily be shown. The form of the curve CD, however, differs from that of the corresponding curves of these hydrogels. Down to -14° , contraction is nearly regular after freezing begins. At this temperature, the ice separating increases and this continues to -20° . From this temperature, no observations could be made till D_1 or D_2 was reached, but the real course of the curve cannot be greatly different from that represented in the figure. The curve DF begins to slope away from DE at -28° , due to melting. The curves show that capillary water in this precipitate is held more firmly

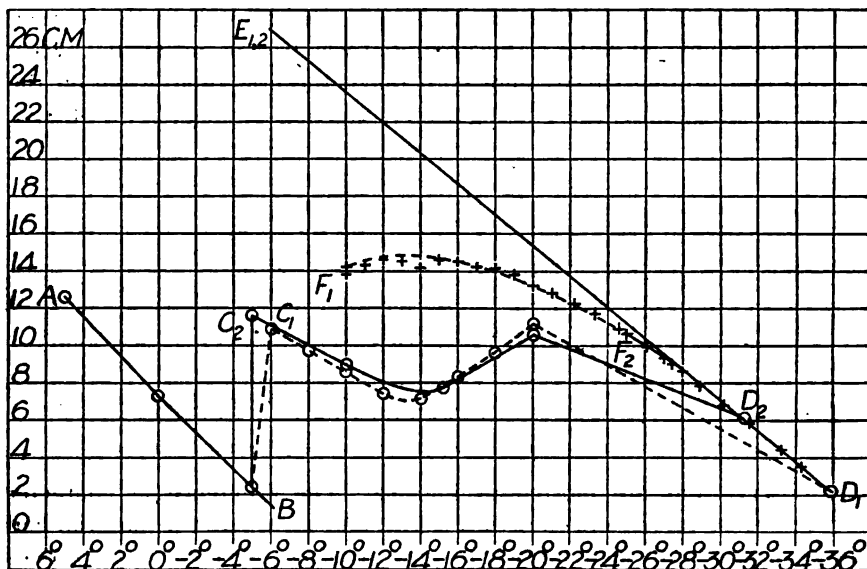


Fig. 13.—Ferric oxide and water.

or in finer capillaries, than in the other colloids investigated. Apparent capillary water was found to be nearly the same on each freezing. It amounted to 0.449 g. per gram of ferric oxide on the first freezing, a value intermediate between the value for silica and alumina. The hydrogel resembles that of silica in there being but little change in capillary water caused by freezing.

The results obtained are in Table VIII. From the form of the curve, it is probable that the results are not as reliable as those for alumina and silica.

TABLE VIII.
Hydrogel of Ferric Oxide.

a. Weight of hydrogel, (g.).	b. Weight of Fe_2O_3 in hydrogel, (g.).	c. Expansion due to free and capillary water, (cm.).	d. Volume of 1 cm., (cc.).	e. Free and capillary water, (g.).	f. Unfrozen water, (g.).	g. Per cent. of unfrozen water $\frac{100f}{b+f}$
9.190	4.178	25.3	0.01064	2.968	2.044	32.4

The percentage of water remaining unfrozen corresponds to the empirical formula $\text{Fe}_2\text{O}_3 \cdot 4.25\text{H}_2\text{O}$.

In view of the results obtained above, which show quite definitely that considerable amounts of water can be frozen from colloidal precipitates after all water in its usual free condition has been removed, it is necessary to correct the conclusions which were drawn by one of us¹ (Foote) regarding the condition of water in hydrogels. A method was developed in the work referred to which showed the point where free water was just removed, and the water remaining was considered to be in solid solution. It is evident, however, that after free water is removed, it will be followed by capillary water, with its lower vapor pressure corresponding to lower freezing point, so that the method is one for determining the amount of combined and capillary water in a hydrogel instead of water in solid solution. For this purpose, the method probably gives more reliable data than any other. The results of the two methods are, however, not strictly comparable, the main reason being that the dilatometer method includes part of the capillary water in the free water, as previously explained, so that the "apparent capillary water" found is less than the capillary water which really exists.

We are indebted to Prof. W. G. Mixter of this laboratory for suggesting the use of lampblack and water in our work.

Work on the freezing of colloids is being continued in this laboratory.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE JEFFERSON PHYSICAL LABORATORY OF HARVARD UNIVERSITY.]

FURTHER NOTE ON BLACK PHOSPHORUS.

By P. W. BRIDOMAN.

Received November 26, 1915.

In a previous number of *THIS JOURNAL*,² I have described a new black modification of phosphorus. It was produced by heating white phosphorus to 200° under a pressure of 12000 kg. or more; attempts to form it by other methods failed. Professor A. Smits, of Amsterdam, who had made such exhaustive studies of the relations between white and red phosphorus, has interested himself in the subject and has made measurements of the vapor pressure of black phosphorus. He has suggested in correspondence that it would be of interest to find the effect of high pressures on red phosphorus in the presence of iodine as a catalyzer. The purpose of this note is to describe this experiment and several others dealing with the same subject—the possibility of changing red to black phosphorus.

"Red" phosphorus is known not to be a definite substance, but varies

¹ *THIS JOURNAL*, 30, 1388 (1908); 31, 1020 (1909).

² *Ibid.*, 36, 1344 (1914).

greatly in appearance and density according to the method of preparation. The varieties close to the upper limits of density are violet in appearance, and are called by Smits "violet" phosphorus. At a definite temperature there is a definite constitution at which violet phosphorus is in internal equilibrium; in this sense violet phosphorus is a definite substance. In the following experiments, two varieties of red phosphorus are to be distinguished; a bright brick red variety formed by heating white phosphorus to a red heat at a pressure of 500 kg. in an atmosphere of nitrogen, and a sample of violet phosphorus, probably much the same as the violet phosphorus of Smits.

The violet phosphorus was made by heating white phosphorus under pressure in the presence of sodium. I discovered quite by accident that metallic sodium is a very efficient catalyzer of the transition from white to violet. The white phosphorus, with a trace of sodium, was subjected to a pressure of 4000 kg. at room temperature, and then heated at constant volume to 200°. The rise of pressure during the rise of temperature was abnormally low, only 500 kg. At 200°, pressure was raised to 12500 kg. for 20 minutes and then to 130000 kg. for 45 minutes. The expected transition to black phosphorus did not occur. The apparatus was then cooled while under pressure, and pressure released at room temperature. The white phosphorus was found entirely transformed to violet. A small piece of the bright red phosphorus which had been placed originally at the bottom of the mass of white phosphorus was quite unaltered in appearance. There can be no question, as shown by the change of pressure, that the change from white to violet took place during the heating at some temperature below 200°. An interesting point not settled by the experiment is as to whether the change to violet takes place above or below the melting point of white phosphorus; at 4000 kg. the melting temperature is about 150°. The density of this violet phosphorus determined by the suspension method was 2.348. This is quite normal. In view of the method of formation, including cooling under high pressure, it is very probable that the violet phosphorus obtained in this way is in a condition corresponding to internal equilibrium at 200° and 12000 kg. The normal value for the density shows that the internal equilibrium conditions at this pressure and temperature cannot be much different from the equilibrium conditions at atmospheric pressure.

A piece of the violet phosphorus formed in this way, together with a piece of the bright red variety, were then subjected to pressure and temperature in the presence of iodine; this is the experiment suggested by Professor Smits. Pressure was raised to 8000 at 20°, temperature raised to 200° at constant volume, and then pressure raised to 12500 for 5½ hours. The cylinder was then cooled and the pressure released. No black phosphorus had been formed. There was no change whatever

of the violet in appearance, but the bright red variety was changed to the same violet as the other. Evidently then, the violet modification is the stable form as compared with the red at 200° between 8000 and 12000 kg.

Two additional attempts to change the bright red phosphorus to black in the presence of sodium were without result; pressure was maintained at 12500 for 3 hours on each of these attempts.

Finally, in the attempt to force red phosphorus to change to black, a piece of red was surrounded by white which was raised to 12500 at 200° until the white was transformed to black, in the regular way. I thought that there was a very slight possibility that if the red were impregnated with white in which the change to black were taking place that the red might, in some way, get carried along by the transition, if the change from red to black is indeed a possible one. This experiment was also without result; the red was found unaltered in the midst of a mass of black. No catalyzer was used for this run; the effect of one would have been to transform the white to violet before reaching the region of formation of black.

During this run I took occasion to determine the precise rate at which white is transformed to black. The results were the same as I have observed qualitatively on every previous occasion; I never happened to make numerical measurements before. After pressure has been raised to something over 12000 at 200° the black phosphorus is never produced instantaneously. There is always a period of preparation extending over from 10 to 30 minutes, during which pressure drops slowly, increasing gradually in speed, until it reaches a critical point at which a cataclysmic transformation of the entire mass to black takes place. In Fig. 1 is plotted the pressure against time before the transition. The total drop of pressure previous to the transition was 400 kg. in 15 minutes; during the transition itself pressure dropped more than 8000 kg. in a few seconds. After the formation of the black with drop of pressure to 4000, pressure was raised again to 11000, the limit of the stroke, with very little or no further drop of pressure. This shows that the change from white to black was practically complete in the first rush.

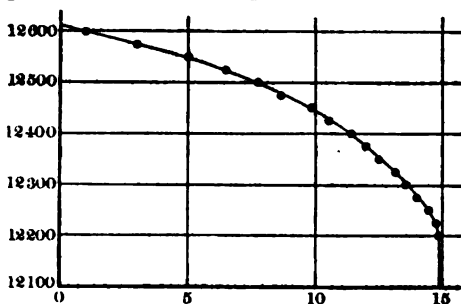


Fig. 1.—Pressure in kg. per cm². against time in minutes immediately before the transition from white to black phosphorus. The sudden drop of pressure shown at the extreme right of the figure, which marked the transition, was of 8000 kg. and took place in a few seconds.

The curve of Fig. 1 throws considerable light on the manner of the transition. Direct change from white to black phosphorus does not take place. Some sort of a preliminary change, involving a decrease of volume, must occur before the transition can run. This change takes place at an accelerated pace at 200° and 12000 kg.; it will not take place with practical velocity at much lower pressures or temperatures. When the preliminary change has reached a certain critical stage, at which the change in density necessary to carry white to black is surely not more than 5% accomplished, the entire edifice becomes unstable and topples over into black phosphorus. It is impossible to say just what this preliminary stage consists of. It is most probable, however, that it is some change uniformly distributed throughout the volume. That this preliminary change is necessary is also suggested by an experiment described in the previous paper; white phosphorus inoculated with black does not transform to black much more easily than when not inoculated.

Unless we are going to admit some phenomenon of molecular momentum, which is almost inconceivable, the fact that pressure during the transition drops to 4000 shows that at pressures even as low as this the black modification is stable compared with the white. The great effectiveness of the preliminary preparation is evident; it enables a transition to run at 4000 which will not start without the preparation at 12000. The experiment further shows that red or violet phosphorus cannot be an intermediate product between white and black. If the phosphorus has passed through violet on its way, it would have stopped there, because we have already seen that the transition from violet to black does not run. Probably the reason why the transition from violet to black does not run under the conditions is because the preliminary stage in the transition does not run; in fact, the preliminary process *cannot* run as an affect of pressure, because the density of the modified white phosphorus from which the black forms itself is less than that of the red phosphorus.

These experiments establish, therefore: (1) that black phosphorus is stable compared with white at 200° at pressures above 4000 kg. and probably at lower pressures; (2) that violet phosphorus is stable compared with white at 4000 kg. and somewhat below 200° , which of course is to be expected; and (3) that violet phosphorus is stable compared with red at 200° at least between 8000 and 12000 kg. The experiments were not able to settle the question as to the relative stability of violet and black at high pressures, because the transition from violet to black could not be made to run, even with catalyzers which are effective for the other phosphorus transitions.

CAMBRIDGE, MASS.

COLLOIDAL SOLID SOLUTIONS.

By D. McINTOSH AND R. EDSON.

Received December 13, 1915.

When a salt solution is reduced gradually in temperature, ice or salt separates until the cryohydric temperature is reached. If the cooling be continued, the precipitation of salt and ice together takes place regularly until the material is changed to a solid. But if the solution be suddenly chilled by liquid air or solid carbon dioxide, the whole mass is quickly frozen without apparent segregation of salt or ice. We propose, in this preliminary paper, to describe some of the properties of these frozen solutions, to which we have given the name of colloidal solid solutions; and we hope in the future, to study their conducting power, their transference ratios and other properties with some care.

The solutions were prepared by plunging a copper tube containing the liquids (and the platinized electrodes when conduction experiments were intended) into a refrigerant, such as carbonic acid and ether. When the solution had reached the temperature of the bath, the tube was removed and dipped for an instant into warm water. The frozen block was pulled out, placed in a test tube, and examined at a convenient temperature.

This frozen material naturally resembled ice, but is more opaque and not so hard. It may be ground to any degree of fineness in a cooled mortar. When examined with a microscope, it appears perfectly homogeneous, and shows no evidence of the formation of ice or salt crystals, so that the particles may be colloidal in size. Analyses of sections from various parts of the solution showed the same composition. If the solid be allowed to melt undisturbed, the salt—except in the case of very strong solutions—dissolves completely. These solutions may be described as “reversible” in comparison with the cryohydrates.

Frozen solutions of this type conduct electricity slightly at low temperatures. When a direct current is employed, the electrodes polarize, and the salt is decomposed as in an aqueous solution. With a 20% solution of potassium iodide at -80° , iodine showed itself instantly when 110 volts were applied. Alkali, of course, was produced during electrolysis.

The resistance of these solutions is large, but decreases rapidly as the temperature rises. A change of 30° may alter the resistance several thousandfold.

When one of these solutions is finely powdered, it gives on melting the exact temperature at which the original liquid would be in equilibrium with pure ice, so that they can be used to maintain any desired temperature. One needs only to prepare a solution freezing at the temperature desired. The solution is then chilled quickly in the manner described. When powdered, it melts exactly at its freezing point, and in a Dewar flask, may be used to maintain a very constant temperature.

It is possible in this way, to prepare constant temperature baths to -40° , using a solution of hydrochloric acid. For lower temperatures, organic liquids might be employed. Mixtures of salts might be used, too, to give constant melting points at high temperatures; but here the choice of materials is so large that this would be of little value.

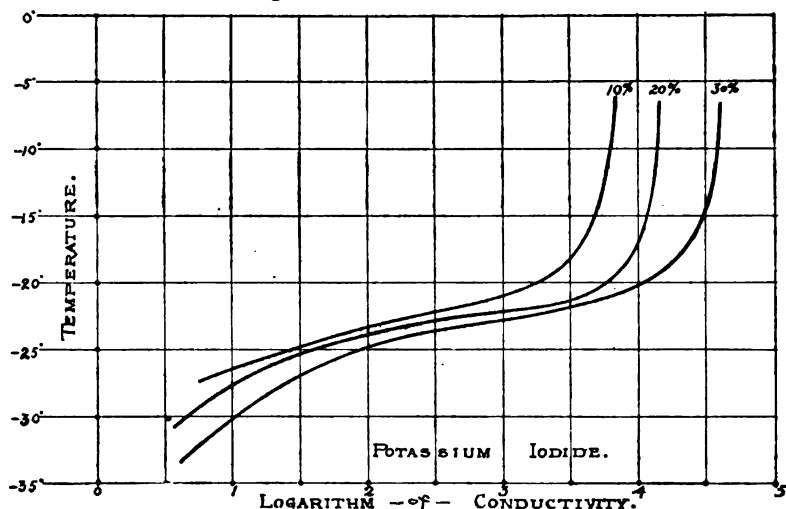


Fig. 1.

We have measured the conductivities at various temperatures of 10, 20, and 30% solutions of potassium iodide in water, and the results are shown in the curves (Fig. 1) where the logarithms of the conductivities

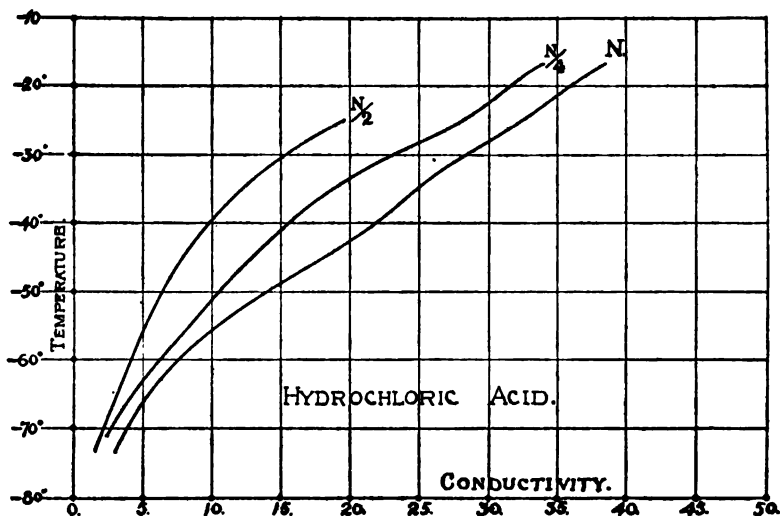


Fig. 2.

are plotted, in order that the results may be shown. A bath of ether and carbon dioxide was used, and with an automatic device it was possible to maintain the temperature within 0.3° of any temperature desired. These frozen solutions are poor conductors of heat, and the temperature must be held constant for at least thirty minutes before measurements can safely be made.

From the actual figures, the conduction is seen to increase most rapidly at about -21° , and as this is the cryohydric temperature for a solution of potassium iodide in water, it seems that even with rapid cooling a certain amount of segregation takes place.

In Fig. 2 the relative conductivities of N , $0.5 N$ and $0.25 N$ hydrochloric acid solutions are shown. These values are plotted directly, the last values being multiplied by 10. The conducting power increases fairly regularly with the temperature, so that there is no evidence of segregation. This is to be anticipated, since the cryohydric temperature for hydrochloric acid and water is far below the temperatures employed. The conductivities of the acid solutions are much greater than those of salt solutions of the same strength.

Until the experiments described here were undertaken, we were unaware that these solutions had been studied. Professor W. D. Bancroft has kindly given us a number of references to articles by Weimarn. We have been unable to consult the originals but the abstracts in the *Centralblatt* do not seem to bear directly on our work.

McGILL UNIVERSITY.

CRYSCOPIC MEASUREMENTS AT LOW TEMPERATURES.

By H. S. REID AND D. MCINTOSH.

Received September 11, 1915.

It has been shown that organic substances containing oxygen, when dissolved in liquefied hydrobromic acid, unite with the solvent forming definite salts melting far above the melting point of either constituent.¹ Ether, for example, gives the compound $C_4H_{10}O.HBr$ melting at -46° , while ether and hydrobromic acid melt at -120° and -86° , respectively. To explain the formation of these salts it has been assumed that the oxygen at the low temperature acts as a tetravalent element, yielding with hydrobromic acid such compounds as $C_4H_{10}O$ $\begin{smallmatrix} \diagup H \\ \cdot \\ \diagdown Br \end{smallmatrix}$ or $C_4H_{10}O = BrH$.

The first of these formulae seems the more probable; for, in a study of the transport numbers,² it was found that the ether, or other organic body,

¹ Archibald and McIntosh, *J. Chem. Soc.*, 85, 919 (1904); McIntosh, *THIS JOURNAL*, 33, 71 (1911); Maass and McIntosh, *Ibid.*, 34, 1273 (1912).

² Steele, McIntosh and Archibald, *Phil. Trans.*, (A) 205, 99 (1905).

under an electric stress moves towards the cathode, *i. e.*, the ether formed part of the positively charged ion.

The measurement of the conductivities of these solutions¹ showed certain anomalies as compared with water solutions, for the molecular conductivities increased with concentration. To account for this, a theory of complexes in solution of the type $(C_4H_{10}O)_x (HBr)_y$ was advanced, so that in these solutions we may have very complex ions. It was proved that this theory of complexes might account for the increase in molecular conductivity with concentration, if it were assumed that two or more molecules of the solute united with the solvent to form a compound which undergoes ionic dissociation.

A careful study of the freezing-point curves from 100% hydrobromic acid to 100% substance containing oxygen, showed that the compounds in solution were largely dissociated into their constituents. In order to explain, if possible, these anomalies, and to throw light on the compounds in solution, we have made a number of determinations of the molecular weights of several oxygen compounds by the freezing-point method, and have worked to somewhat greater concentrations than are usual in these measurements.

Previous molecular-weight determinations were made by Steele, McIntosh and Archibald² by the boiling-point method, but their apparatus was probably defective. The most recent work has been done by Beckmann and Waentig,³ but not much could be learned of the molecular structure of the compounds formed, on account of irregular results and also because they worked only at low concentrations.

Preparation and Purification of Reagents.

The reagents used as solutes were toluene, chloroform and carbon tetrachloride, which behave, as we shall show, normally in liquid hydrobromic acid, and methyl alcohol, ethyl alcohol, ether, acetone, ethyl acetate, acetic acid, paraldehyde and acetaldehyde, which form compounds with liquid hydrogen bromide. Bromine was also used as a solute in order to ascertain its solubility in the solvent, since on this point there is conflicting evidence.

The hydrogen bromide was made by dropping bromine into red phosphorus and water, passing the gas through water containing red phosphorus, then through phosphorus pentoxide and condensing it by solid carbon dioxide and ether.

The methyl and ethyl alcohol were purified by distillation, drying over calcium oxide and redistilling, drying over anhydrous copper sulfate and again distilling.

¹ Archibald, *THIS JOURNAL*, 29, 665, 1415 (1907).

² *Loc. cit.*

³ *Z. anorg. Chem.*, 67, 17 (1910).

The ether was distilled, allowed to stand over sodium and redistilled.

The acetone was crystallized from sodium bisulfate solution; a solution of sodium carbonate was added, the acetone distilled off, dried over calcium chloride and redistilled.

The ethyl acetate was washed with a solution of sodium chloride and sodium carbonate, separated, distilled, dried over calcium chloride and redistilled.

The acetic acid was obtained by repeated freezing of glacial acetic in the ordinary way.

The pure paraldehyde was distilled and converted into the acetaldehyde by adding a drop of concentrated sulfuric acid and distilling.

The toluene had been previously purified and had stood over sodium for several years.

The chloroform was distilled, washed with water and dried over concentrated sulfuric acid.

The carbon tetrachloride was washed with a caustic soda solution, distilled, dried over calcium chloride and redistilled.

The bromine was dried by distilling from barium oxide in a glass apparatus.

Apparatus.

The apparatus used was much the same as that employed by Beckmann and Waentig. The thermometer was a platinum resistance one made by Heraeus in which the platinum was embedded in the quartz, thus enabling the thermometer to take up the temperature of the solution very quickly. The main difference between our apparatus and that used by Beckmann and Waentig was in the position of the electromagnet. They attached their magnet directly to the inner glass tube, but we placed ours above the tube, so that the thermometer wires were not cut by the magnetic lines, and thus disturbances in the galvanometer were avoided.

Fig. 1 shows a cross section of

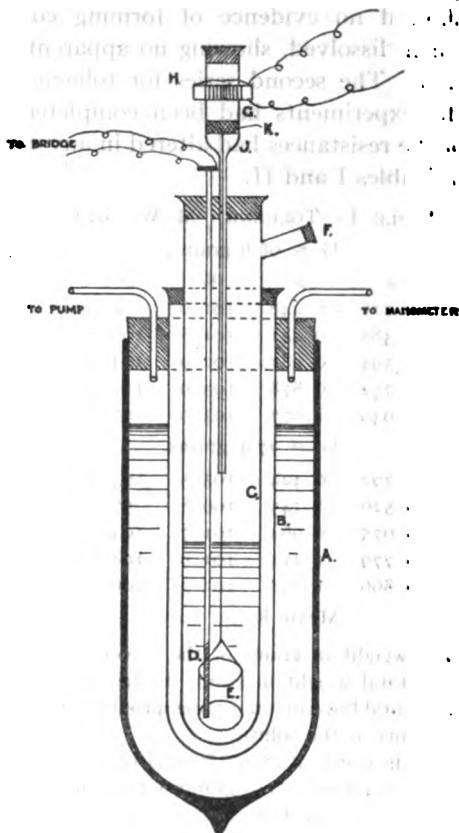


Fig. 1.

the large Dewar flask A used. B is a glass tube immersed in the carbon dioxide and ether. C is the freezing-point tube containing the platinum resistance thermometer D, and platinum stirrer E. F is the side tube through which the solute was introduced. G is a glass tube reaching into A, carrying the stirrer and electromagnet H. J is the iron ring which is attracted by the magnet and so lifts and lowers the stirrer. The pressure used corresponded to a temperature of from -90° to -92° .

The electrical measuring apparatus was of the Carey-Foster type and consisted of two 3000 ohm resistances connected in series with a bridge wire, and two balancing resistances boxes. A Broka galvanometer was used, and at the freezing point of hydrobromic acid one mm. on the bridge wire corresponded to 0.00158° . All the resistances were calibrated before and after the experiments.

Procedure.

In order to find the value of K, the constant for hydrogen bromide, we used as solutes toluene, chloroform and carbon tetrachloride, which showed no evidence of forming compounds. They behaved normally when dissolved, showing no apparent tendency to association or dissociation. The second series for toluene and chloroform was made after all the experiments had been completed, in order to make sure that none of the resistances had altered in any way. The results obtained are shown in Tables I and II.

TABLE I.—TOLUENE. M. W. = 92.8.

G = 96.6 grams.

g.	Δ .	K.	K'.
0.218	0.248	101.0	101.0
0.385	0.441	101.8	102.8
0.594	0.687	102.9	104.9
0.752	0.878	103.9	107.4
0.930	1.077	103.0	97.0

G = 77.4 grams.

g.	Δ .	K.	K'.
0.292	0.424	103.5	103.5
0.526	0.745	100.8	97.6
0.675	0.964	101.7	104.5
0.779	1.114	101.9	104.6
0.866	1.244	102.3	106.3

Mean K = 102.3.

G = weight in grams of the solvent.
 g = total weight in grams of the solute.
 Δ = total lowering in degrees produced by grams of the solute.
 K = the constant $\times 10^{-3}$ found from lowering of Δ degrees by g grams of the solute.
 K' = constant the $\times 10^{-3}$ found from the individual measurements.

TABLE II.—CHLOROFORM. M. W. = 119.5.

G = 67.9 grams.

g.	Δ .	K.	K'.
0.218	0.284	105.8	105.8
0.421	0.541	104.2	102.5
0.565	0.723	103.8	102.6
0.755	0.975	104.8	107.6
0.955	1.239	105.2	107.2

G = 80.7 grams.

g.	Δ .	K.	K'.
0.200	0.219	105.5	105.5
0.412	0.433	101.3	97.6
0.622	0.669	103.8	108.6
0.797	0.860	104.1	105.2
0.891	0.967	104.7	109.3

Carbon Tetrachloride, M. W. 154.0.

G = 59.5 grams.

g.	Δ .	K.	K'.
0.358	0.389	101.7	101.7
0.577	0.633	101.9	102.1
0.770	0.847	101.9	101.7
0.940	1.039	102.1	103.5
1.109	1.234	102.8	105.9

Mean K = 103.9.

From these results the mean value of K is seen to be 103.1. This value was used throughout the remainder of the work to calculate the molecular weights of the solutes employed.

The latent heat of fusion, W , of hydrogen bromide can be calculated, knowing K , from the formula

$$K = 0.02T^2/W \text{ and is equal to 6.79 cal. per g.}$$

Table III shows the results obtained using ethyl alcohol as the solute. Care had to be exercised in introducing the alcohol because of the large heat of combination, which caused the alcohol to be sprayed on the walls of the tube unless added very slowly. The alcohols appeared to be most reactive, but the other solutes forming compounds with the solvent also had to be added slowly.

TABLE III.—ETHYL ALCOHOL. $K = 103.1$. TABLE IV.—METHYL ALCOHOL. $K =$

M. W. = 46.				103.1. M. W. = 32.			
$G = 71.0 \text{ grams.}$				$G = 60.4 \text{ grams.}$			
g.	Δ .	M.	M'.	g.	Δ .	M.	M'.
0.107	0.140	111.0	111.0	0.200	0.309	110.5	110.5
0.238	0.287	117.7	129.9	0.406	0.601	115.2	118.4
0.589	0.723	118.2	116.8	0.642	0.978	112.2	107.0
0.964	1.265	110.6	100.6	0.812	1.313	105.4	86.7
1.164	1.546	109.3	103.5	1.054	1.664	108.1	118.0
1.436	1.929	108.0	103.2	1.305	1.988	112.2	132.1
1.674	2.334	104.3	84.5	1.565	2.335	114.3	127.5
1.816	2.592	102.0	80.0	1.764	2.486	121.3	225.1
$G = 86.6 \text{ grams.}$				2.023	2.651	130.4	265.4
0.167	0.196	101.3	101.3	2.486	3.515	120.3	90.6
0.346	0.384	107.0	113.7	$G = 68.0 \text{ grams.}$			
0.540	0.588	109.3	113.1	0.197	0.278	107.7	107.7
0.837	0.918	108.0	107.0	0.335	0.471	108.1	108.5
1.029	1.100	111.2	125.7	0.464	0.651	108.1	108.8
1.243	1.302	113.7	126.1	0.670	0.936	108.5	109.7
1.585	1.678	112.5	108.2	0.828	1.121	112.2	129.2
1.914	2.148	106.0	83.5	1.045	1.435	110.5	104.7
2.097	2.341	106.5	112.9	1.251	1.719	110.5	110.1
2.401	2.794	102.3	79.9	1.437	1.929	113.0	134.5
2.658	3.144	100.4	87.6	1.661	2.223	113.5	115.2
2.975	3.597	98.5	83.3	1.816	2.407	114.3	127.5
				2.025	2.618	117.0	148.6
				2.199	2.873	115.7	102.7
				2.452	3.320	111.8	85.2
				2.597	3.525	111.4	106.5

In dilute solutions the alcohol is polymerized 2.3 to 2.4 times. The amount of association increases very slightly until a concentration of 1.4 to 1.8 per cent. is reached where the amount of the association is 2.5. At further concentration the molecular weight decreases quite rapidly. This seems to show that at this concentration the amount of dissociation

becomes very much greater and doubtless continues to increase, because the association would increase with greater concentration, and the amount of dissociation must be greater than the association in order to give a lower molecular weight. This view is also supported by the fact that the molecular conductivity of alcohol in hydrogen bromide increases with concentration. Table XI shows the variation in the molecular weight and molecular conduction¹ with concentration. It will be seen that the concentration where the molecular weight begins to decrease, corresponds fairly well with the concentration where the first marked bend occurs in the conductivity curve, *i. e.*, where the dissociation first becomes marked.

Table IV shows the results obtained with methyl alcohol. The association is here seen to be greater than in the case of ethyl alcohol. Taking the results in the second part of the table, it is seen that in dilute solutions the amount of association is 3.4. The increased association is very small indeed, but it seems to reach a maximum at a concentration of 3.0%, where the amount of association is 3.6. With increased concentration the association seems to decrease a little.

As in the case of ethyl alcohol, the amount of dissociation must be quite marked after a concentration of 1.0% has been reached, as is shown by the conductivity curve. Therefore the association must be much more marked than in the case of the ethyl alcohol. The compounds formed with alcohol were found by Maass and McIntosh² to be $\text{CH}_3\text{HO.HBr}$ and $\text{C}_2\text{H}_5\text{O.HBr}$.

The results obtained with ethyl acetate are shown in Table V.

In very dilute solutions there appears to be a certain amount of dissociation, but very little. With increasing concentration the association steadily increases until the percentage of the acetate is about 3.0 when the amount of association is 1.6. On addition of more of the solute the value of the molecular weight decreases, showing that the amount of dissociation has increased.

No measurements of molecular conductivity are available, but it is more than probable that the same explanation would apply here as in the case of the alcohols. The compounds formed were found to be $\text{CH}_3\text{COOC}_2\text{H}_5\text{HBr}$, $(\text{CH}_3\text{COOC}_2\text{H}_5)_2(\text{HBr})$, and $\text{CH}_3\text{COOC}_2\text{H}_5(\text{HBr})_4$.³

Table VI shows the values obtained for the molecular weight of ether.

In dilute solutions the ether seems to be associated 1.2 times. The molecular weight is constant until a concentration of 1.5% has been reached where the amount of association increases slightly, and then gradually decreases with increasing concentration indicating increased dissociation.

¹ Archibald, *Loc. cit.*

² *Loc. cit.*

TABLE V.—ETHYL ACETATE. $K = 103.1$.

M. W. = 88.

 $G = 78.4$ grams.

g.	Δ .	M.	M'.
0.102	0.167	80.6	80.6
0.321	0.483	87.4	91.0
0.483	0.683	93.0	106.6
0.661	0.842	113.3	147.6
1.035	1.105	123.3	187.1
1.353	1.305	136.5	209.1
1.683	1.494	148.3	230.3
2.051	1.855	145.5	134.3
2.401	2.202	143.3	132.5
2.605	2.457	139.5	107.5

 $G = 68.2$ grams.

g.	Δ .	M.	M'.
0.176	0.317	83.9	83.9
0.334	0.520	97.0	117.6
0.569	0.804	106.8	125.0
0.845	1.131	112.8	127.5
1.013	1.302	117.4	148.6
1.217	1.400	131.2	312.0
1.475	1.629	136.7	170.7
1.845	2.023	137.8	142.0
2.192	2.389	138.5	143.2
2.619	2.939	134.2	115.8
2.930	3.451	128.0	91.1
3.030	3.656	122.0	73.2

TABLE VI.—ETHYL ETHER. $K = 103.1$.

M. W. = 74.

 $G = 75.4$ grams.

g.	Δ .	M.	M'.
0.177	0.278	87.2	87.2
0.340	0.522	89.1	91.2
0.501	0.785	87.3	83.7
0.712	1.123	86.5	84.6
0.832	1.301	87.3	92.4
1.157	1.712	92.3	117.6
1.361	1.872	99.4	189.5
1.624	2.303	96.4	90.7
1.797	2.546	96.5	105.8
2.136	3.092	94.3	91.5
2.376	3.556	91.1	76.3
2.481	3.891	89.3	65.7

 $G = 59.5$ grams.

g.	Δ .	M.	M'.
0.304	0.612	86.1	86.1
0.480	0.962	86.6	87.2
0.609	1.203	87.8	92.8
0.755	1.372	85.5	150.0
0.936	1.611	100.8	131.4
1.125	2.009	97.1	82.2
1.226	2.223	95.6	81.0
1.542	2.789	95.6	95.7
1.759	3.203	94.9	90.1
1.909	3.525	93.5	79.9
2.286	4.241	93.0	90.4

No conductivity measurements are available here. Ether forms the compounds $(C_2H_5)_2O \cdot HBr$ and $(C_2H_5)_2O \cdot (HBr)_2$.

Acetone in solution gives the values for the molecular weight shown in Table VII.

The association in dilute solutions is quite marked, and is equal to 1.5, increasing quite rapidly until a concentration of 2.2% has been reached, where the amount of association is 3. With increasing concentration the molecular weight gets steadily less, showing that the dissociation is greatly increased. The only compound formed was found to be $C_2H_5O \cdot HBr$.

Table VIII gives the results obtained with acetic acid.

In this case it was difficult to obtain concordant results on account of the high freezing point of the acid, which caused the drop coming in contact with the thermometer or stirrer to solidify immediately. The hydrogen bromide was rotated as far as possible up the sides of the tube to dissolve any adhering particles.

The association here is very marked and in dilute solutions is almost equal to 2. The association increases rapidly with concentration, having a value of nearly 5 at a concentration of 3%. Until this concentration is attained there seems to be no tendency for the dissociation to exceed

the association. Acetic acid forms a compound¹ with hydrobromic acid, but the ratio of the two acids has not been obtained with certainty.

TABLE VII.—ACETONE. $K = 103.1$. TABLE VIII.—ACETIC ACID. $K = 103.1$.

M. W. = 58.				M. W. = 60.			
G = 71.6 grams.				G = 72.8 grams.			
g.	Δ .	M.	M'.	g.	Δ .	M.	M'.
0.172	0.340	72.9	72.9	0.286	0.321	126.4	126.4
0.362	0.540	96.7	137.1	0.659	0.484	192.9	324.1
0.570	0.683	120.2	208.8	1.230	0.643	270.6	511.5
0.944	0.937	145.2	212.2	1.825	0.828	311.4	453.2
1.127	1.056	153.9	221.7	G = 70.0 grams.			
1.497	1.230	175.5	306.0	0.222	0.314	104.2	104.2
1.891	1.551	175.5	176.7	0.455	0.597	114.5	126.1
2.208	1.908	166.8	127.7	0.745	0.724	154.4	337.8
G = 63.1 grams.				1.137	0.851	199.7	456.9
0.190	0.301	100.3	100.3	1.477	0.940	234.2	563.0
0.466	0.580	131.4	167.3	1.862	1.050	264.2	516.2
0.844	0.853	161.9	226.3	2.152	1.146	280.0	446.0
1.182	1.079	178.2	244.2				
1.383	1.246	181.4	197.3				
1.681	1.565	175.5	153.1				
1.958	1.886	170.0	141.0				
2.186	2.259	158.4	99.9				
2.374	2.598	149.2	90.7				
2.760	3.377	133.3	80.3				

The molecular weights of paraldehyde and acetaldehyde are shown in Table IX.

The paraldehyde compound even in dilute solutions seems to be dissociated to a considerable extent and the dissociation increases with concentration. There seems to be no tendency to association, which is to be expected as the paraldehyde is already associated.

The results with acetaldehyde are interesting since the molecular weights found agree well enough with those obtained for the paraldehyde to show that the acetaldehyde is at once polymerized to paraldehyde by the hydrogen bromide.

Table X shows the results obtained with bromine as the solute.

They prove that bromine is soluble in liquid hydrobromic acid, and that the bromine behaves normally, showing no tendency to association or dissociation. It seems to be a simple case of solution, the bromine existing as Br_2 and probably not uniting with the solvent.²

Maass and McIntosh³ found bromine to be insoluble in liquid hydrogen bromide, probably on account of the frozen bromine taking a measurable time to dissolve. Beckmann and Waentig³ also found bromine only

¹ THIS JOURNAL, 30, 1103 (1908).

² Compare chlorine and hydrochloric acid, *Loc. cit.*

³ *Loc. cit.*

TABLE IX.—PARALDEHYDE. $K = 103.1$.

M. W. = 132.			
G = 83.5 grams.			
ϵ .	Δ .	M.	M'.
0.174	0.209	103.0	103.0
0.350	0.415	104.2	105.3
0.599	0.769	95.8	86.1
0.737	0.983	92.3	79.6
1.083	1.451	91.9	91.5
1.462	2.141	84.2	67.8
1.916	2.967	79.6	67.9

G = 76.2 grams.			
0.174	0.266	88.4	88.4
0.524	0.790	89.7	90.5
0.782	1.203	88.0	84.6
1.133	1.719	89.0	92.0
1.501	2.402	84.6	73.0
1.850	3.092	81.0	68.4
2.118	3.587	79.9	73.3

ACETALDEHYDE. M. W. = 44.

G = 73.3 grams.			
0.173	0.250	97.3	97.3
0.382	0.566	94.8	92.9
0.568	0.866	92.5	87.4
0.854	1.339	89.8	85.2
1.130	1.800	88.3	84.3
1.584	2.489	89.6	92.7
1.892	3.013	88.3	82.1

TABLE X.—BROMINE. $K = 103.1$.

M. W. = 160.			
G = 66.9 grams.			
ϵ .	Δ .	M.	M'.
0.217	0.225	148.5	148.5
0.347	0.360	148.0	147.7
0.493	0.504	150.3	155.6
0.814	0.777	161.0	181.0
1.123	1.023	168.7	193.0

G = 68.0 grams.			
0.195	0.185	159.5	159.5
0.397	0.374	161.0	162.4
0.628	0.576	165.3	173.4
0.807	0.754	162.4	152.9

very slightly soluble in liquid hydrobromic acid, and to give it a light brown color. On the other hand two Dutch investigators, whose paper we have unfortunately misplaced, have plotted the freezing-point curve, bromine—hydrogen bromide, and have found the bromine readily soluble in the liquefied acid. We found it quite soluble and also that the color of the solution changed from light brown to deep red with increasing concentration.

TABLE XI.

	Dilution.	Assoc-iation.	Mol. conduc-tivity $\times 10^3$.		Dilution.	Assoc-iation.	Mol. conduc-tivity $\times 10^3$.
C_2H_5OH	5.00	2.35	0.502	C_2H_5O	5.00	2.26	0.34
	3.33	2.35	0.605		3.33	2.50	0.77
	2.00	2.47	1.002		2.00	3.07	1.40
	1.66	2.44	1.310		1.66	3.13	2.32
	1.25	2.30	2.464		1.35	3.03	3.24
	1.00	2.22	4.650		1.07	2.90	4.30
CH_3OH	5.00	3.38	0.685	CH_3COOH	5.00	2.00	18.4
	3.33	3.38	0.820		3.33	2.50	44.8
	2.00	3.39	1.660		2.00	3.30	123.0
	1.66	3.50	2.385		1.66	4.00	171.0
	1.25	3.45	4.710		1.25	5.00	252.0
	1.00	3.53	9.250				

Summary.

We have learned something of the molecular complexity of the substances used when dissolved in liquid hydrogen bromide. With the exception of paraldehyde, which is already associated, all the substances forming compounds with the solvent were found to be both associated and dissociated, the amount of association varying very much according to the substances used. Up to the present, no method has been devised for measuring the amount of dissociation of these substances in solution, so that the true amount of association cannot be found. In dilute solutions, however, the amount of association as found will be very nearly correct because of the low value of the molecular conductivity in these solutions.

The relationship between the amount of association and the molecular conductivity seems to agree with the theory enunciated. Figures for the molecular conductivities of ethyl and methyl alcohol,¹ acetic acid,² and acetone³ in liquid hydrogen bromide alone are available, and, as shown by Table XI, the solutes showing the greatest amount of association in solution have the greatest molecular conductivity. Acetic acid has an abnormally high conductivity. This may be due to the presence of hydrogen ions as well as the complex ions. Except in dilute solutions it also shows the greatest tendency to association.

A comparison of the properties of ether, alcohol, etc., dissolved in liquid chlorine with the same compounds in hydrobromic acid can now be made. Oxonium compounds are formed in both cases, and a study of the slopes of the freezing curves in systems such as hydrobromic acid—ether and chlorine—ether shows that in solution these compounds are largely broken down into their constituents. Solutions in chlorine, however, are non-conductors, *i. e.*, exhibit no electrolytic dissociation. The determination of molecular weights in this solvent made recently by P. Waentig and one of us⁴ show normal results for ether over a considerable concentration, while methyl and ethyl alcohol are greatly polymerized. We have, then, complex systems where the compounds are partially broken down into their constituents further complicated by association and in some cases, electrolytic dissociation. It seems impossible at present to assign these three factors their proper proportion, and to give formulae to the oxonium compounds.

The increase in complexity in solution shown by the increasing values of the molecular weights and the rapid increase in molecular conductivity, points to the correctness of the view previously expressed,

¹ THIS JOURNAL, 29, 665 (1907).

² *Ibid.*, 29, 1415 (1907).

³ *Loc. cit.*

⁴ *Trans. Roy. Soc., Canada*, 1915.

that the ions are much more complex than would be expected from the oxonium theory.

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[CONTRIBUTION FROM THE BIOCHEMIC DIVISION, BUREAU OF ANIMAL INDUSTRY, U.
S. DEPARTMENT OF AGRICULTURE.]

THE DECOMPOSITION OF TETRATHIONATES IN ALKALINE SOLUTION AS A SOURCE OF ERROR IN CERTAIN IODINE TITRATIONS.¹

BY ROBERT M. CHAPIN.

Received January 17, 1916.

It has long been known that tetrathionates are not stable. Particularly has Gutmann² shown that sodium tetrathionate rapidly reacts with moderately concentrated hot caustic soda to form sodium thiosulfate and sodium sulfite. But that the reaction might progress with significant rapidity in cold and dilute solutions seems to have remained unsuspected; at any rate, no allowance is made for such a possibility in certain methods of quantitative analysis. For example, it is a very common procedure to determine arsenic in a variety of materials by some modification of the process described by Williamson.³ Iodine resulting from the use of hydriodic acid as a reducing agent is removed by sodium thiosulfate, following which the solution is in practice frequently rendered decidedly alkaline before being brought to the proper condition for titration.

Some time ago, following the official directions of the Assoc. Offic. Agr. Chemists⁴ for the estimation of "total arsenious oxide" in insecticides and fungicides, the writer became impressed with the fact that the method, as laid down, did not afford the uniformly accurate results promised by the theory of the process. He found that substitution of sodium sulfite for thiosulfate as a discharging agent for iodine produced a distinct improvement in results and acted accordingly in work⁵ in which accuracy was particularly necessary. Later, incidental to other work,⁶ he showed that tetrathionates are in fact rather rapidly affected by exposure at room temperature to comparatively low concentrations of hydroxyl ions. The purpose of the present paper is to extend these observations sufficiently to form a guide to correct procedure in iodometric methods, etc., involving the conditions outlined.

Tetrathionate solution (0.0519 *N*) was prepared by titrating iodine

¹ Published by permission of the Secretary of Agriculture.

² *Ber.*, 40, 3614 (1907).

³ Sutton, "Volumetric Analysis," 10th Edition, p. 156.

⁴ *Bur. of Chemistry, Bull. 107* (Revised), Reprint January 18, 1912, p. 25.

⁵ *J. Ind. Eng. Chem.*, 6, 1002 (1914).

⁶ *Ibid.*, 8, 151 (1916).

solution (0.1022 *N*) with sodium thiosulfate solution (0.1054 *N*), without starch. Portions of 20 cc. of tetrathionate solution were measured into flasks, diluted, and mixed with measured amounts of solutions of alkalis or alkaline salts, the final volume in each case being 100 cc. The temperature of the laboratory and solutions was somewhat over 30°. The mixture in each flask was left standing 15 minutes, after which it was acidified with dilute hydrochloric acid and methyl orange, then titrated with standard iodine and starch.

Character of medium.	Cc. 0.1022 <i>N</i> iodine.	Character of medium.	Cc. 0.1022 <i>N</i> iodine.
Blank.....	1 drop	NH ₄ OH, 0.1 <i>N</i>	0.95
NaOH, 0.1 <i>N</i>	9.21	NaHCO ₃ , 0.5 <i>N</i>	2 drops
NaOH, 0.01 <i>N</i>	3.98	NaHCO ₃ , 0.1 <i>N</i>	1 drop
Na ₂ CO ₃ , 0.1 <i>N</i>	5.20	NaHCO ₃ , 0.5 <i>N</i> , plus ¹ CO ₂ ..	1 drop
Na ₂ CO ₃ , 0.01 <i>N</i>	0.50		

It is clear that tetrathionates are notably sensitive to even low concentrations of hydroxyl ions, though only slightly affected by sodium bicarbonate, and still less by sodium bicarbonate in presence of carbonic acid. It therefore follows that acid solutions containing tetrathionates, if to be later titrated with iodine, or subjected to any treatment involving assumption that the tetrathionate present has remained unaffected, should never be neutralized by any substance of distinctly alkaline properties. Significant errors may not necessarily result, but a source exists which can produce grave errors through incautious manipulation. Sodium bicarbonate within reasonable limits of excess is appropriate, provided the solution be not left at an elevated temperature a considerable length of time. As a discharging agent for iodine, under such conditions as prevail in the determination of arsenic, it seems safer to abandon the use of thiosulfate altogether, and to substitute therefor a dilute solution of sodium sulfite—about 0.5% of the anhydrous salt.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF MINNESOTA.]

NONIDEAL SOLUTIONS. THE ACTIVITY OF A DIFFICULTLY SOLUBLE COMPONENT.

By E. K. STRACHAN.

Received March 29, 1915.

I. Introduction.

The study of the colligative properties of solutions has been greatly facilitated by use of the concept of the ideal solution.² This concept

¹ (50 cc. *N* NaHCO₃ saturated with CO₂ before added to diluted tetrathionate.)

² E. W. Washburn, *THIS JOURNAL*, 32, 660 (1910); G. N. Lewis, *Z. physik. Chem.*, 61, 129 (1907).

has rendered unnecessary the restriction that the solution be dilute, a limitation which was necessarily imposed on all discussions in this field as long as the van't Hoff gas law hypothesis of osmotic pressure was the only one employed. By use of the ideal solution law it is possible to express accurately the colligative properties of an ideal solution in terms of the concentrations of its components. However, the ideal solution law yields quantitative results only when applied to ideal solutions. This very greatly limits its usefulness in dealing with the majority of solutions employed in scientific and technical work. There is, therefore, need of a systematic study of nonideal solutions to the end that quantitative relations between their colligative properties and composition may be discovered.

At the outset it is important to note that deviations from the ideal solution law can be attributed to either or both of two causes: first, the number of molecular species in the solution is different from the number of components, that is, association, dissociation, or a combination of solvent and solute has taken place; and second, the thermodynamic nature of the solution is different from that of the components. Consideration of the first factor is aside from the purpose of this article, since if the number of molecular species and amount of each in the solution were known, the ideal solution law could be applied, provided the last-named cause of deviation played no part. The second factor is frequently called "change in the nature of the medium" or "change in the thermodynamic environment." Solutions exhibiting effects of this latter sort only, form the subject of this paper, and may be termed truly nonideal.

The simplest of such nonideal solutions seems to be one consisting of a solid of only moderate solubility dissolved in a normal liquid forming a mixture in which the number of molecular species is equal to the number of components. Obviously such a solution is not an ideal one as its components are only partially miscible. Were it ideal, however, Henry's law would apply to it, and the desired relation of partial pressure to concentration would be

$$p = (N/N_s) p_o, \quad (1)$$

in which p is the partial pressure of the solute when its mol fraction in the liquid is N , p_o is the vapor pressure of the pure solute, and N_s its mol fraction in a saturated solution. Probably a somewhat similar law governs the behavior of nonideal solutions.

No direct measurements of the partial pressures of a system of the sort described above exist in the literature. However, it is possible to obtain the necessary data by a process of calculation in the case of certain solutions. Those of iodine in carbon tetrachloride, carbon disulfide, and bromoform are particularly suited to this purpose, as they show no associa-

tion, dissociation, or solvation¹ and so may be regarded as truly nonideal.

II. Data and Calculations.

These calculations are based on the fact that the coefficient of distribution of a substance between two solvents is the ratio of its concentration in each when its partial pressure is the same from both. As the ratio of distribution of iodine between water and each of the above solvents has been determined, it is necessary to know only the rate of change of the vapor pressure with the concentration in water in order to be able to calculate it for each of the other solvents. Now, the vapor pressure of iodine from a saturated solution is equal to its sublimation pressure at the same temperature. Hence, by combining the solubility data with those for the sublimation pressure, one obtains the vapor pressure of iodine from its solution at a number of concentrations, each, however, at a different temperature. These values of the vapor pressure can all be reduced to a common temperature by use of the Clausius equation, provided the latent heat of vaporization of iodine from the solution be known. This latter is equal to the difference between the heat of solution and the heat of sublimation, and these in turn can be obtained respectively from the solubility by use of the van't Hoff equation, and from the sublimation-pressure data by use of the Clausius equation.

Table I summarizes the results of these calculations. The solubilities shown in Col. 2 were obtained from the results of Fedotief,² Hartley and Campbell,³ Sammet,⁴ and Jakovkin⁵ by graphical interpolation. The

TABLE I.—SUBLIMATION PRESSURE AND SOLUBILITY DATA.

1. Temperature. T.	2. Solubility. Mols/liter × 10 ³	3. Heat of soln.	4. Subl. press. pT.	5. Heat of subl.	6. Heat of vaporization. L _v .	7. Vap. press. at 25°. p ₂₅ .
0	0.650	...	0.030	0.150
	...	4.50	...	16.12	10.44	...
10	0.871	...	0.085	0.210
	...	4.74	...	14.58	10.22	...
20	1.159	...	0.205	0.250
	...	5.34	...	14.74	9.60	...
30	1.567	...	0.469	0.360
	...	5.86	...	14.70	9.08	...
40	2.188	...	1.025
	...	6.50	...	14.82	8.44	...
50	3.020	...	2.154
	...	7.00	...	14.66	7.94	...
60	4.188	...	4.266	—
			Mean,	14.94		

¹ Beckman, *Z. physik. Chem.*, 58, 559 (1907).

² *Z. anorg. Chem.*, 69, 30 (1910).

³ *J. Chem. Soc.*, 93, 741 (1908).

⁴ *Z. physik. Chem.*, 53, 648 (1905).

⁵ *Ibid.*, 18, 590 (1895).

sublimation-pressure data are those of Baxter and Hickey.¹ The latent heat of vaporization of iodine from its aqueous solution, obtained by subtracting the latent heat of solution (Col. 3) from the latent heat of sublimation (Col. 5), is shown in Col. 6, and can be expressed with sufficient accuracy by the equation $L_v = (26950 - 58 T)$ small calories. Now iodine solutions of the concentrations shown in Col. 2 of the table must have the vapor pressures shown in Col. 4 at the temperatures which appear in Col. 1. By use of the Clausius equation, $dp/dT = L_v/vT$, one can calculate what vapor pressure these solutions would have at any common temperature, say 25°. On substituting the value of L_v obtained above and integrating, it takes the form

$$\log p_{25} = \log p_T + 19.77 (298 - T)/T - 29.20 \log 298/T.$$

Col. 7 of the table shows the values of the partial pressure of iodine at 25° obtained by substituting the proper values of p and T in this equation. The figures in Col. 2 of Table II were obtained from these by graphical interpolation.

TABLE II.

Conc. in water ml.-limols per liter.	Partial pressure iodine.	Distribution coefficient.			Concentration in millimols per liter in			Mol-fraction $\times 10^4$ in				C for			
		CCl ₄ .	CS ₂ .	CHBr ₃ .	CCl ₄ .	CS ₂ .	CHBr ₃ .	CCl ₄ .	CS ₂ .	CHBr ₃ .	Water.	CCl ₄ $\times 10^{-1}$.	CS ₂ $\times 10^{-1}$.	CHBr ₃ $\times 10^{-1}$.	H ₂ O $\times 10^{-1}$.
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.
0.1	0.025	85.06	585	438	8.5	58.5	43.8	8.28	35.4	38.9	0.018	3.3	2.8	3.0	5
0.2	0.047	85.08	586	443	17.0	117.2	88.4	16.53	71.0	78.0	0.036	2.5	2.1	2.3	3
0.4	0.094	85.10	592	458	34.0	236.8	183.0	33.7	143.0	162.0	0.072	2.1	2.4	2.2	3
0.5	0.118	85.15	599	466	42.6	299.5	233.0	41.5	181.0	205.0	0.090	3.5	2.6	2.3	4
0.6	0.141	85.21	608	476	51.1	364.8	286.0	49.8	220.0	251.0	0.108	3.4	2.5	2.2	4
0.8	0.187	85.70	631	497	68.5	504.8	397.0	66.8	304.0	347.0	0.144	3.3	2.3	2.2	5
1.0	0.232	86.76	651	519	86.7	651.0	519.0	84.6	392.0	450.0	0.180	3.9	2.0	2.2	6
1.2	0.276	88.37	666	541	106.0	781.0	650.0	102.5	467.0	560.0	0.216	4.0	3.4	2.3	(10)
1.34	0.305	120.0	905.0	745.0	116.0	544.0	644.0	0.244
Mean, 3.2 2.6 2.2 4															

The relation of vapor pressure to concentration for solutions of iodine in the other solvents can now be calculated by use of the distribution coefficient. It is important to note, however, that the distribution coefficient is a function of the concentration even in solutions such as these in which there is no change of molecular complexity, a characteristic to be expected, of course, of a nonideal solution. Hence, the values of the distribution coefficient obtained experimentally by Jakovkin² and by Washburn and Strachan³ were plotted against the concentration of iodine

¹ THIS JOURNAL, 29, 127 (1907).

² Z. physik. Chem., 18, 588 (1895).

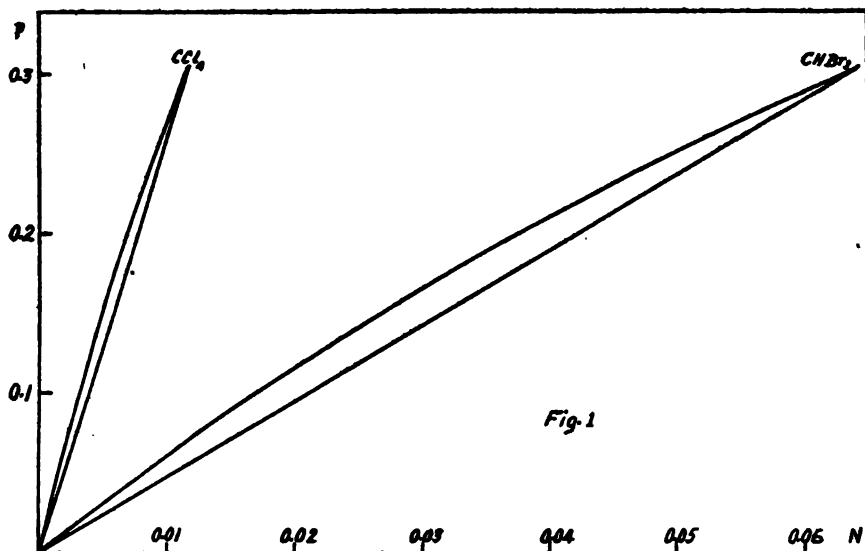
³ THIS JOURNAL, 35, 689 (1913).

in the aqueous solution, and a smooth curve drawn through the points so obtained. The value of the distribution coefficient corresponding to any desired concentration could thus be read off the curve. The values of the distribution ratio shown in Cols. 3, 4 and 5 of Table II were obtained in this way. These were multiplied by the figures in Col. 1 in order to obtain the concentrations of iodine in the other solvents, the results appearing in Cols. 6, 7 and 8. The mol-fraction of iodine in each of these solutions was calculated on the assumption that the volume of the solution was the sum of the volumes of its components. Although this is not strictly in accord with the facts, the error involved is too small to affect the ultimate conclusions. The mol fractions obtained in this manner are shown in Cols. 9 to 12 of Table II.

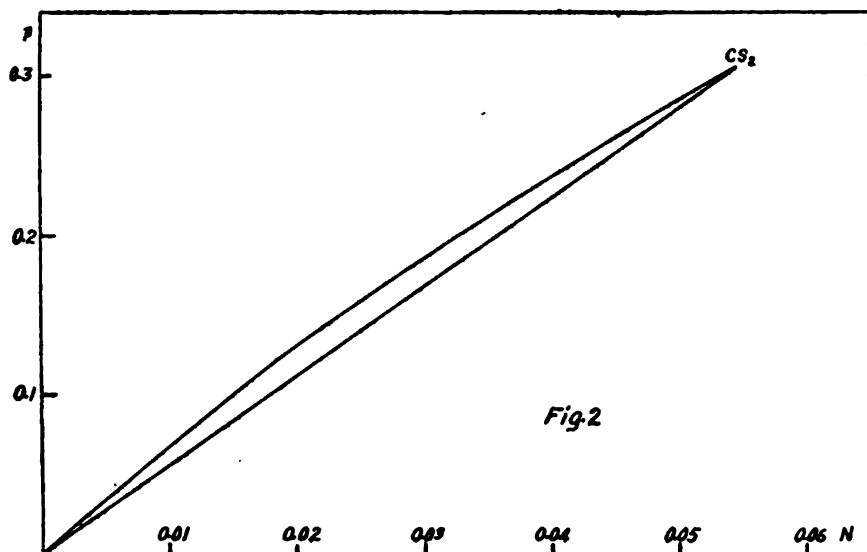
The partial pressures shown in the table can be expressed by the equation

$$p = N/N_s p_o + C(N_s - N)N, \quad (2)$$

in which C is an empirical constant and the other letters have the significance already assigned to them. Cols. 13 to 16 show the values of C for each of the four solutions. They are remarkably constant for each solution within the limits of error of the data. Although water, on account of its high degree of association, does not belong to the class of solutions under discussion, for the sake of comparison its constant was calculated. The solubility of iodine is so small in this case that the molecular complexity of the solution is not noticeably altered. Equation 2 differs from Henry's law (Equation 1) only by the term $C(N_s - N)N$. The magnitude of this correction term can be seen by inspection of Figs.



1 and 2, where the mol fraction of iodine in the solutions is plotted against its partial pressure. The curved lines represent the values calculated from the experimental data and represent Equation 2, while the straight



lines were obtained by use of Henry's law. The curve for water is omitted, as the deviation from Henry's law would be apparent only in a very large figure.

III. Discussion of Results.

It is worthy of note that the value of C is in every case almost inversely proportional to the square of the solubility of iodine in the solution, the proportionality constant being 9×10^{-2} for bromoform, 8×10^{-2} for carbon disulfide, 4×10^{-2} for carbon tetrachloride, and 2×10^{-2} for water. The decrease in these four values of the proportionality constant with the solubility may be accidental, or may be due to the increase of the mol-fraction of solvent as that of the solute decreases. However, the agreement is very close, considering that the solubility of iodine in the different solvents varies more than 10^5 -fold, and its square, more than 10^{10} -fold. It further suggests that Equation 2 is the limiting form approached by a more general expression when the solubility becomes sufficiently small, and is not a mere power-series interpolation formula. Investigations are now in progress in this laboratory to determine the relation of vapor pressure to concentration prevailing in other nonideal solutions, and to inquire into the exact significance of the constant C . It is hoped that thus a more general equation may be obtained expressing vapor pressure or activity in terms of concentration.

This equation is important not merely because it relates vapor pressure to concentration for this type of nonideal solution, but rather because it can be used to express thermodynamic activity¹ or "active mass" in terms of concentration. Consequently, any property of a solution of this type which can be expressed in terms of thermodynamic activity can also be expressed in terms of concentration. This fact is of especial value in the discussion of chemical equilibria in solutions of this sort, as they constitute one of the most common and interesting types. In such cases, the mass-action law, depending as it does on Henry's law, cannot express the equilibrium relations accurately, except at infinite dilution or when compensation effects are present. But by combining this equation with the laws of thermodynamics it is possible to determine the relation which must exist between the mol-fractions of the reacting substances in an equilibrium mixture in this kind of a solution.

In a qualitative way this equation shows that the distribution coefficient will increase with increasing concentration, if the concentration of solute in the solution in which it is most soluble is placed in the numerator, provided both solutions are truly nonideal. This conclusion agrees with the available data, not only for the particular systems employed in this article, but also quite generally. It shows at once that not all cases of inconstancy of the distribution ratio can be attributed to change of molecular complexity of the solute, and, as a corollary, that inconstancy of the distribution ratio is not a sufficient basis for concluding that a solute has different molecular weights in the different solvents. This, of course does not exclude change of molecular complexity from also being a cause of variation of the distribution ratio with the concentration.

IV. Summary.

(1) The partial pressure of a difficultly soluble component from its solution in several solvents has been calculated.

(2) The partial pressure of a difficultly soluble component of a truly nonideal solution can be expressed by the relation

$$p = (N/N_s) p_o + C(N_s - N)N$$

in which p is the partial pressure of the solute when its mol fraction is N , p_o is the vapor pressure of the pure solute, and N_s its mol fraction in a saturated solution.

(3) C is a constant approximately inversely proportional to the square of the solubility.

MINNEAPOLIS, MINN.

¹ As defined by Lewis (*Z. physik. Chem.*, 61, 129 (1907)) for these solutions the activity, $\xi = N/RT [P_o/N_s + C(N_s - N)]$ if the vapor is a perfect gas.

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF THE UNIVERSITY OF WISCONSIN.]

THE PARTITION COEFFICIENTS OF HYDROGEN PEROXIDE BETWEEN WATER AND CERTAIN ORGANIC SOLVENTS.

BY JAMES H. WALTON AND HAROLD A. LEWIS.

Received January 19, 1916.

The fact that hydrogen peroxide is soluble in ether and amyl alcohol has been recognized for a long time. It is not generally known, however, that a surprisingly large number of organic solvents dissolve this substance. A. Brann¹ carried out a series of semi-quantitative experiments in this laboratory, in which he agitated equal volumes of hydrogen peroxide solutions with various organic solvents at room temperature, and determined the amount of peroxide in each phase. The results of his experiments are incorporated in Table I. Brann found that the peroxide

TABLE I.

Solvent.	Conc. in solvent Conc. in water	Solvent.	Conc. in solvent Conc. in water
Ethyl acetate.....	2/5	Chloroform.....	1/600
Nitrobenzene.....	1/200	Benzene.....	1/200
Acetophenone.....	1/4	Isobutyl alcohol.....	1/3
Amyl acetate.....	1/8	Propyl formate.....	1/8
Ethyl isovalerianate.....	1/40	Isobutyl butyrate.....	1/50
Isoamyl propionate.....	1/12	Propyl butyrate.....	1/30

is also soluble in many other organic solvents, notably phenol and aniline. His experiments show that the solvents that dissolve water will also dissolve hydrogen peroxide.

Measurements of the partition coefficients of hydrogen peroxide have been made by Calvert² with amyl alcohol and water and by Osipoff and Popoff³ with water and ether at 17.5°.

The results obtained by the latter investigators are as follows:

Vol. ether.....	1	1	2	5	6	7	8	9	10	
Vol. water.....	2	1	1	1	1	1	1	1	1	
Conc. H ₂ O ₂ in water	17.4	16.8	16.7	16.7	13.3	13.5	14.9	14.3	13.9
Conc. H ₂ O ₂ in ether									

Experimental.

The hydrogen peroxide used in these experiments was Merck's "Perhydrol." The organic liquids were the purest materials obtainable. These were redistilled once, and in some cases twice, and the constant boiling fractions used.

An electrically heated and controlled thermostat was constructed in which to carry on the experiments at constant temperature. Equal volumes of water and the given solvent, usually 15 cc. of each, and the de-

¹ *Dissertation*, University of Wisconsin, 1914.

² *Z. physik. Chem.*, 38, 513 (1901).

³ *J. Russ. Phys. Chem. Soc.*, 35, 637 (1903).

sired volume of hydrogen peroxide were pipetted into glass stoppered bottles of about 60 cc. capacity. These bottles were then clamped in the bath in a shaking device. The liquids in the bottles were allowed to come to the temperature of the bath, and then were shaken until equilibrium was reached, about an hour being the usual period necessary. After equilibrium was reached, definite volumes of each layer were pipetted off and diluted. In general, 10 cc. of the aqueous layer were diluted to 200 cc. with distilled water. The layer of organic solvent was diluted with ethyl alcohol, either 5 or 10 cc. being made up to 100 cc., depending upon the ease of separation of the layers and upon the concentration of peroxide. Aliquot portions were then taken and the concentration of hydrogen peroxide in each solution was determined.

Two methods were employed for the estimation of the hydrogen peroxide. Whenever possible, it was titrated with standard potassium permanganate in dilute sulfuric acid solution. In these cases the sulfuric acid was added during dilution. In general 20 cc. portions were titrated,

TABLE II.
Partition Coefficients of Hydrogen Peroxide between Water and Certain Organic Solvents at 25°. Determined by Titration Method.

Solvent.	Solvent and water taken cc. of each.	Cc. 30% H_2O_2 taken.	Titration of 1 cc. of:		Partition coefficient $\frac{C_{aq.}}{C_s}$.
			Solvent C_s . ¹	Water $C_{aq.}$ ¹	
Ethyl acetate.....	10.0	5.0	11.75	46.25	3.94
	10.0	5.0	13.77	53.84	3.92
	10.0	5.0	14.39	57.14	3.97
	10.0	5.0	14.25	57.24	4.01
	10.0	7.0	13.20	53.20	4.03
	15.0	5.0	10.01	39.68	3.97
	15.0	5.0	10.03	39.60	3.95
	15.0	7.0	13.28	54.44	4.10
	15.0	7.0	13.27	54.50	4.10
	15.0	7.0	13.00	53.51	4.11
Isobutyl alcohol.....	15.0	5.0	15.96	41.13	2.58
	15.0	7.0	20.18	52.30	2.59
	15.0	5.0	16.60	43.62	2.63
	15.0	7.0	21.05	54.13	2.58
Amyl acetate.....	15.0	5.0	3.64	47.75	13.1
	15.0	7.0	4.59	60.65	13.2
	15.0	10.0	5.90	76.80	13.0
Acetophenone.....	15.0	5.0	7.77	46.46	5.98
	15.0	7.0	9.82	59.47	6.06
	15.0	10.0	11.15	64.78	5.82
Ether.....	15.0	3.0	3.22	29.32	9.11
	15.0	5.0	5.05	44.22	8.76
	15.0	7.0	6.90	56.90	8.25

¹ C_s and $C_{aq.}$ represent concentration of H_2O_2 in 1 cc. of solvent and aqueous layers, respectively, expressed in terms of cubic centimeters of approximately 0.1 N $KMnO_4$.

so that the number of cubic centimeters of permanganate used gave the value for 1.0 cc. of the original aqueous layer.

In several cases permanganate could not be used because it oxidized the organic solvent. Consequently a gasometric method was devised to determine the concentration of peroxide. In this method an aliquot part of the solution was placed in a flask connected by a capillary tube to a water-jacketed gas buret. A capsule of manganese dioxide, held in the neck of the flask by a glass rod, was released, and allowed to drop into the liquid.¹ The manganese dioxide decomposed the hydrogen peroxide completely in about fifteen minutes. The volume of oxygen liberated was read on the gas buret. Errors of reading were decreased to the minimum by the use of large portions of the solution. Table II, preceding, gives the results obtained from use of the titration method with those liquids in which the hydrogen peroxide underwent no change of molecular weight.

In the above table it will be seen that the coefficient for ethyl acetate was determined a number of times more than for any of the other liquids. This was done to make sure that the method employed would give constant results. In the case of isobutyl alcohol, amyl acetate, and acetophenone, constant results were obtained. That the hydrogen peroxide does not undergo association in any of the solvents used in Table II is evidenced by the fact that the values $C_{aq.}/C_s$ for the different concentrations are constant.

The partition coefficients for water-ether are lower than the lowest value obtained by Osipoff and Popoff, 13.9. These investigators, however, worked at 17.5°, whereas the above measurements were carried out at 25°. In order to see whether or not this difference was due to the difference in temperature, partition coefficients were determined at 0°, with the following results:

Vol. ether.	Vol. water.	Vol. 30% H ₂ O ₂ .	$C_{aq.}$	C_s	$\frac{C_{aq.}}{C_s}$
15 cc.	15 cc.	5 cc.	35.15 cc.	6.00 cc.	5.85
15 cc.	15 cc.	7 cc.	45.3 cc.	7.95 cc.	5.72

These results indicate that for lower temperatures the value of the partition coefficient decreases. Consequently the values obtained in this investigation are appreciably lower than those of Osipoff and Popoff.

A number of other organic solvents were used, but for various reasons quantitative results could not be obtained. Phenylhydrazine dissolves hydrogen peroxide, but it is rapidly oxidized with the formation of aniline as one of the oxidation products. With methyl iodide the solubility was so small that the buret readings were not reliable. By titration of the aqueous layer the $C_{aq.}/C_s$ was found to be approximately 200. *m*-Tolui-

¹ Walton, *Z. physik. Chem.*, 47, 2 (1904).

dine forms an addition product with the sulfuric acid. The titration of the aqueous layer gives a value of C_{aq}/C_s that is about 5. Aniline and phenol showed very little oxidation by the hydrogen peroxide, but were so rapidly oxidized by the permanganate that concordant results could not be obtained. The layers were consequently analyzed by the gasometric method already described. The results are given in Tables III and IV.

TABLE III.

Distribution of Hydrogen Peroxide between Water and Aniline. Temperature 25°.

Vol. aniline.	Vol. water.	Vol. 30% H ₂ O ₂ .	Oxygen from 2 cc. aniline C _s .	Oxygen from 2 cc. aqueous layer C _{aq} .	$\frac{C_{aq}}{C_s}$.
15 cc.	15 cc.	1 cc.	2.80 cc. ¹	11.40 cc. ¹	4.08
15 cc.	15 cc.	2 cc.	5.10 cc.	20.90 cc.	4.10

TABLE IV.

Distribution of Hydrogen Peroxide between Water and Phenol. Concentrations Expressed in Millimols per 10 cc. Temperature 25°.

H ₂ O ₂ in phenol C _s .	H ₂ O ₂ in aqueous layer C _{aq} .	$\frac{C_{aq}}{C_s}$.	$\frac{C_{aq}}{\sqrt{C_s}}$.
105.7	459.1	4.35	44.7
182.1	839.0	4.61	62.1
250.5	1217.0	4.88	76.9
337.2	1868.0	5.55	102.0

The constancy of the values C_{aq}/C_s shows that the hydrogen peroxide does not undergo association when dissolved in aniline. The corresponding values obtained in Table IV, which gives the solubility of hydrogen peroxide in phenol, are far from constant, and indicate association. If the association consists in doubling all the molecules of hydrogen peroxide, the value $C_{aq}/\sqrt{C_s}$ should be constant, but this is not the case.

TABLE V.

Distribution of Hydrogen Peroxide between Water and Quinoline. Concentrations are in Millimols per 10 cc.

Temp.	H ₂ O ₂ in quinoline. C _s .	H ₂ O ₂ in aqueous layer. C _{aq} .	$\frac{C_{aq}}{C_s}$.	$\frac{C_{aq}}{\sqrt{C_s}}$.
0°.....	617	170.1	0.276	6.85
	1636	522.6	0.319	12.9
	2419	944.5	0.391	19.2
25°.....	1118	408.0	0.365	12.2
	1456	635.0	0.435	16.6
	2181	1090.0	0.505	23.4
	2715	1538.0	0.559	29.5
	3361	2157.0	0.642	37.2
40°.....	1330	686.0	0.516	18.7
	1993	1197.0	0.602	26.8

The solubility of hydrogen peroxide in quinoline is interesting because the partition coefficient is less than one; in other words, when quinoline

¹ At 20° and 740 mm.

is agitated with an equal volume of hydrogen peroxide solution it removes more than half the hydrogen peroxide. The results of experiments with quinoline which are given in Table V point to association, for the ratio $C_{aq.}/C_s$ is not constant. The values of $C_{aq.}/\sqrt{C_s}$ and of $C_{aq.}/\sqrt{C_s}$ have also been computed, but they do not give constants.

An examination of the data for the distribution at 0° , 25° and 40° , respectively (Table V), shows the existence of an appreciable temperature coefficient. For a given concentration of hydrogen peroxide, the lower the temperature the greater the percentage dissolved by the quinoline. A temperature effect of so great a magnitude is unusual for substances for which constant values of the partition coefficient can be obtained. Cases similar to the above have been found, however, by Hantzsch¹ and his co-workers. The large temperature coefficient, and the great change in distribution for a change in the concentration, indicate a combination of the solute with one of the solvents.² In the case of quinoline the existence of a compound of quinoline and hydrogen peroxide dissolved in the quinoline layer, and in equilibrium with uncombined hydrogen peroxide seems very probable, particularly when one recalls the basic properties of quinoline and the slightly acid properties of the peroxide. Quinoline, moreover, shows an unusual tendency to form addition products with a surprisingly large number of compounds. The results obtained from hydrogen peroxide and phenol are doubtless due to similar causes.

This investigation, and in particular the reactions of quinoline solutions of hydrogen peroxide, is being continued.

Summary.

1. Organic solvents that dissolve water will also dissolve hydrogen peroxide.

2. The partition coefficient of hydrogen peroxide between water and each of the following substances has been determined at 25° : ethyl acetate; isobutyl alcohol; amyl acetate; acetophenone; ethyl ether; aniline. The hydrogen peroxide does not undergo association in these solvents. The values obtained for ethyl ether do not agree with those of Osipoff and Popoff.

3. Hydrogen peroxide is soluble in phenol and in quinoline. The quinoline is not a solution of simple peroxide molecules, but probably consists of a compound of the solvent and hydrogen peroxide in equilibrium with hydrogen peroxide.

4. Quinoline is an unusually good solvent for hydrogen peroxide.

¹ Hantzsch and Seboldt, *Z. physik. Chem.*, 30, 258 (1899); Hantzsch and Vagt, *Ibid.*, 38, 705 (1901).

² Herz, "Der Verteilungssatz," *Ahrens' Sammlung*, Vol. 15, p. 17.

At 0° for certain concentrations of hydrogen peroxide the κ value $\frac{\text{H}_2\text{O}_2 \text{ in water}}{\text{H}_2\text{O}_2 \text{ in quinoline}}$ may be as low as 0.276.

MADISON, WISCONSIN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN.]

THE OXIDATION OF MANGANESE SOLUTIONS IN PRESENCE OF THE AIR.

By VICTOR LENHER.

Received January 21, 1916.

It is well known that manganous solutions when neutralized undergo hydrolysis, and that when such solutions are allowed to stand in contact with the air, oxidation takes place with the precipitation of hydrated manganese dioxide. In the presence of the common alkalies, manganous salts yield manganous hydroxide, which when exposed to the air undergoes oxidation with the formation of hydrated manganese dioxide.

The deposition of pyrolusite, the most plentiful of the manganese ores in nature, is doubtless the result of a series of reactions of neutralization and oxidation. Manganese is presumably transported in nature as bicarbonate, sulfate, or chloride. When a manganese-bearing solution comes in contact with such a substance as calcium carbonate which is so widely distributed in nature, the manganese salt is neutralized, hydrolysis takes place, the action of the oxygen of the air steps in and manganese dioxide is precipitated, the calcium carbonate serving to neutralize the free acid which is liberated in the reaction.

In studying the reactions incident to the deposition of manganese dioxide by the neutralization of manganese salts and the subsequent oxidation by means of air, a series of observations have been made by the writer which at first sight seemed to be examples of certain principles of positive and negative catalysis.

A large number of glass tubes were cleansed with the utmost care and in each tube was placed a 1% solution of pure manganous chloride, a piece of Iceland spar, and a piece of metal, mineral or metallic compound. The solution and solids filled about one-fourth of the tube; the remainder of the space was occupied by air. These tubes were then sealed and allowed to stand for a long time in order to allow the slow oxidation by the air to take place. Very striking differences in behavior are exhibited by the various metals under these conditions. Certain of the metals cause the production of manganese dioxide to be accelerated, while others cause its formation to be retarded, or in some cases to be actually inhibited. Lead and bismuth accelerate the deposition of manganese dioxide from a manganese chloride solution when calcite is present as a neutralizing agent.

In blank experiments made with only manganese chloride solution and Iceland spar, the first noticeable separation of manganese dioxide appears only after standing for several weeks. With metallic lead present in the solution, a greater amount of the dioxide separates out overnight than in several weeks in the blank experiments. Certain other metals, such as tin, arsenic and antimony, prevent this oxidation of the manganese with formation of manganese dioxide. In fact they inhibit it entirely.

Such metals as mercury, copper, zinc, nickel, cobalt, cadmium, silver, gold, as well as mercuric sulfide, millerite, pyrite, chalcopyrite, and zinc blende, are without any effect in this reaction, the tubes at the end of a number of months of action appearing to be identical with those in which only the manganese solution and Iceland spar were present.

The acceleration of the oxidation of the manganese by the oxidation with air in presence of lead is not necessarily dependent on the presence of the metal itself, since lead sulfide, carbonate or sulfate also accelerate this reaction; nor is the reaction dependent on the use of the chloride of manganese, inasmuch as the sulfate or acetate of manganese also works equally well.

The retardation of this oxidation in the presence of metallic antimony, arsenic or tin, is readily explained by the reducing action of their salts toward manganese dioxide. The alkaline stannites, arsenites and antimonites reduce manganese dioxide; consequently in their presence it cannot be produced. The lack of reaction cannot, therefore, be regarded in the light of a negative catalysis.

Further, the presence of a higher oxide or salt of a higher oxide of these elements is without any appreciable effect on the reaction. Thus, in the presence of an arsenate, stannic oxide, or antimonie oxide, the oxidation and subsequent deposition of manganese dioxide proceeds in the same way as though these substances were absent.

The presence of a reducing substance when a neutralized solution of manganese is exposed to the air, impedes the oxidation and formation of manganese dioxide, or actually prevents it. Such substances which in general are not reducing in character, as the common metals mercury, copper, cadmium, zinc, cobalt, silver, and the minerals cinnabar, millerite, pyrite, chalcopyrite, sphalerite, magnetite, hematite, corundum, bauxite and ilmenite, are without apparent influence on this oxidation.

Lead and lead compounds accelerate this oxidation greatly; bismuth and bismuth compounds also accelerate the oxidation, but to a lesser degree than lead.

From our numerous experiments along these lines, it is apparent that in the laboratory lead and lead compounds act as a great accelerator in the production of manganese dioxide when we attempt to imitate the

agencies which apparently go on in nature in the formation of manganese deposits.

Thus far, however, no regular association of lead with the oxidized manganese minerals has been noted in the field, so far as the writer is aware.

MADISON, WIS.

[FROM THE DEPARTMENT OF CHEMISTRY, PRINCETON UNIVERSITY.]

THE USE OF HYDROFLUORIC ACID IN THE SEPARATION OF SOME HEAVY METALS FROM TIN, ANTIMONY, TUNGSTEN, AND MOLYBDENUM, BY MEANS OF THE ELECTRIC CURRENT.

By LEROY W. MCCAY AND N. HOWELL FURMAN.

Received January 22, 1916.

About a year ago one of us (M.) showed that from a nitrohydrofluoric acid solution of copper, lead, tin, and antimony, the last two metals being in the higher state of oxidation, the electric current precipitates the copper and lead only, the former at the cathode, the latter as the peroxide at the anode.¹ It was stated then that, under similar conditions, silver and mercury can be separated from tin and antimony. Considerable experimental work has convinced us that the separation of silver and mercury from tin and antimony is as complete and their subsequent determination as exact as was observed in the case of copper and lead. The silver deposits contain no weighable amounts of platinum, which fact we attribute to the very weak currents necessarily employed in order to obtain compact silver deposits. The mercury deposits, however, usually contain a little platinum, as had already been noted in the case of copper deposited from nitrohydrofluoric acid solutions.² The amount found is variable, but seems to increase with the quantities of tin and hydrofluoric acid present, and with the time during which the current acts. When the current strength was as high as 3 A., and a Classen rotating anode was employed, the amount of platinum found in the mercury deposits was about 0.0005 g.; in one case 0.0007 g. On treating the deposits with nitric acid the platinum remains in the form of a black powder, or dark and very thin film, and can be rapidly and accurately determined, and the necessary correction made.

Since nitrohydrofluoric acid solutions of tungstic and molybdic acids behave toward the current like those of stannic and antimonie acids, copper, lead, silver and mercury can be separated from tungstic and molybdic as well as from mixtures of stannic, antimonie, tungstic and molybdic acids. The results for silver, copper and mercury are very satisfactory.

¹ THIS JOURNAL, 36, 2375 (1914).

² *Loc. cit.*

The lead peroxide deposited from nitrohydrofluoric acid solutions always weighs more than when precipitated from nitric acid solutions containing no hydrogen fluoride. The excess in weight is from 1-4 mg. The error can be eliminated, and results obtained equal almost in accuracy to those arrived at when lead is determined as the peroxide in nitric acid solutions alone, by proceeding as follows:

After removing the liquid over a deposit and washing it, water containing the necessary amount of nitric acid is poured into the dish until the deposit is just covered, and the current is reversed. In a few minutes solution is complete, the current is once more reversed and the lead reprecipitated as the peroxide. Since, however, it is a well-established fact that even when lead is deposited as the peroxide from nitric acid solutions alone the calculated results are apt to be high, we have found it best, when a high degree of accuracy is desired, either to dissolve the peroxide in a few cubic centimeters of dilute nitric acid containing a little pure hydrogen peroxide, evaporate the solution to dryness in a porcelain crucible, ignite the residue and weigh the lead as oxide, or to convert the nitrate so obtained into the sulfate, the latter being collected and ignited in a Brunck or Neubauer crucible placed in a larger one of porcelain. We have succeeded in detecting fluorine in the lead peroxide deposited from nitrohydrofluoric acid solutions. No quantitative determinations of the fluorine have thus far been made, but the device employed in testing for the element has yielded such satisfactory results that we are assured it is not water alone, but fluorine in addition, which occasions the overweights of the lead peroxide.

The metals and other substances employed in our work were the best furnished by a well-known German firm. The copper, silver, tin, antimony, and lead nitrate had already been examined and found to be practically free from impurities. The mercury was purified by letting it fall in a very thin stream through a long column of dilute nitric acid. It was then distilled three times. The tungstic and molybdic anhydrides were thoroughly digested in boiling concentrated nitric acid, the acid was almost entirely removed by evaporation, the residues were taken up with water, filtered off, washed with nitric acid water and dried at about 250°. No traces of the presence of any heavy metals could be detected in these preparations.

Standard solutions of some of these materials were prepared and convenient amounts pipetted out as required. The necessary solutions of tin and antimony were always obtained by dissolving known weights in a little warm nitrohydrofluoric acid in a platinum dish covered with a piece of platinum foil. When a solution contained antimony, that portion remaining in the lower state of oxidation was converted into the

higher by means of a slight excess of potassium bichromate.¹ The solutions so prepared were then diluted to about 100 cc. and electrolyzed. During the passage of the current the platinum dishes were covered with split clock glasses heavily paraffined, or with pieces of hard rubber shaped like clock glasses and provided with a narrow slit extending from the center to the circumference. When relatively high amperages were used and the anode was rotated, a cover of thin platinum foil was substituted for the one of hard rubber or paraffined glass. This proved to be necessary, for the heat melted the paraffin, and the hot acid spray attacked the rubber. The cover was made by subjecting two semicircular pieces of freshly annealed platinum foil to considerable pressure in a concave and grooved mold. The resulting corrugations render the metal rigid, so that there is no danger of the cover losing its clock-glass shape.

The liquids over the deposits were siphoned off with a short piece of black rubber tubing, upon which the nitrohydrofluoric acid has practically no action. The washing was performed in the ordinary way, the main liquids and washings being trapped in a large ceresin beaker.

Experimental.

Separation of Silver from Tin and Antimony.—Weighed amounts of the metals were placed in an ordinary Classen dish of 125 cc. capacity, 20 cc. nitric acid (1 part acid sp. gr. 1.42 : 5 parts water) and 1 cc. hydrofluoric acid (48%) were added, the dish was covered with a piece of platinum foil and the liquid very gently warmed until all was in solution. The antimony in the lower state of oxidation was then brought to the higher by means of a slight excess of potassium bichromate, the contents of the dish were diluted to 100 cc., and the current was applied.

Sb, 0.1021 to 0.1075 g.; Sn, 0.2001 to 0.2091 g.; E. M. F., 2 volts; Time, overnight.

Current, ampere.....	0.07	0.10	0.05	0.05	0.05
Gram Ag taken.....	0.0271	0.0211	0.0200	0.0175	0.0185
Gram Ag found.....	0.0267	0.0208	0.0197	0.0171	0.0180

The deposits adhered well to the dish, but they were not bright in appearance. Better deposits were obtained by using a Winkler gauze electrode. The solutions were made in a platinum dish and then poured into a ceresin beaker.

Vol. 250 cc., containing 40 cc. 1 : 5 HNO₃, 2 cc. 48% HF and Sb, 0.2113 to 0.3462 g.; Sn, 0.2032 to 0.3098 g.; E. M. F., 2 volts; Time, overnight.

Current, ampere.....	0.05	0.03	0.03	0.03	0.03
Gram Ag taken.....	0.0190	0.0313	0.0326	0.0303	0.0321
Gram Ag found.....	0.0186	0.0311	0.0323	0.0299	0.0320

One of us (F.) made the following determinations in a solution of unknown concentration as to silver. The silver was deposited on a gauze electrode and under the above conditions.

¹ THIS JOURNAL, 36, 2376 (1914).

Sb, 0.1997 to 0.2032 g.; Sn, 0.1060 to 0.1166 g.; E. M. F., 2 volts; Time, overnight.

Current, ampere.....	0.05	0.03	0.03	0.03
Ag, taken.....	25 cc. of soln.			
Gram Ag.....	0.0323	0.0326	0.0325	0.0322

The solution was prepared by dissolving 0.2616 g. pure silver in a little nitric acid and diluting to 200 cc., so that 25 cc. = 0.0327 g. Ag.

Separation of Mercury from Tin and Antimony.—8.0603 g. of pure, redistilled mercury were dissolved in about 15 cc. of concentrated nitric acid, and diluted to a liter. In 25 cc. portions the mercury was determined (1) in nitric acid solution alone, and (2) in nitrohydrofluoric acid. The deposits were washed with alcohol and ether, and dried in a vacuum desiccator over calcium chloride. The desiccator also contained a small vessel full of mercury.

Taken, 0.2015 g. Hg; 20 cc. HNO_3 (1 : 5); Current, 0.5 amp.; E. M. F., 3 volts; Time, overnight; Vol., 100 cc.

Cc. HF (48%).....	0.0	0.0	0.5	
Gram Hg found.....	0.2017	0.2016	0.2017	

The tin and antimony were first dissolved in a platinum dish, covered with a piece of platinum foil, in 20 cc. of nitric (1 : 5) and 5 cc. hydrofluoric acids, the solution being hastened by the application of a very gentle heat. The solution of mercury was then run in from a pipet, any antimony in the lower state of oxidation converted into the higher by means of a slight excess of a saturated solution of potassium bichromate, the volume of the liquid brought to about 100 cc., and the current applied.

Hg taken, 0.2015 g.; Sn, 0.1863 to 0.2124 g.; Sb, 0.0857 to 0.1162 g.; E. M. F., 3 volts; Time, overnight.

Current, ampere.....	0.50	0.50	0.45	0.40	0.50
Gram Hg found.....	0.2018	0.2016	0.2014	0.2017	0.2012
Subtract Pt found.....	0.0002	0.0001

A series of determinations in which roughly twice as much antimony and one-half as much tin were taken, yielded results fully as accurate as those just given.

Vol. 100 cc., containing 20 cc. HNO_3 (1 : 5) and 5 cc. HF and Hg taken, 0.2015 g.; Sn, 0.1005 to 0.1087 g.; Sb, 0.1998 to 0.2262 g.; E. M. F., 3 volts; Time, overnight.

Current, ampere.....	0.45	0.45	0.30	0.25	0.30
Gram Hg found.....	0.2014	0.2013	0.2010	0.2020	0.2016
Subtract Pt found.....	0.0001	0.0001	0.0004

Equally good results for mercury were obtained by using as little as 1 cc. of hydrofluoric acid.

Vol. 100 cc., containing 20 cc. HNO_3 (1 : 5) (except in (5) where 30 cc. were used).

Hg taken, 0.2015 g.; Sn, 0.2004 to 0.2141 g.; Sb, 0.1023 to 0.1170 g.; E. M. F., about 3 volts; Time, overnight.

Current, ampere.....	0.45	0.45	0.40	0.40	
Gram Hg found.....	0.2014	0.2015	0.2018	0.2016	0.2012
Subtract Pt found.....	0.0002	0.0001	0.0002	0.0003	0.0002

The method was subjected to further variations in the amounts of mercury, tin, antimony, etc., the following results being obtained:

Sn, 0.2066 to 0.4000 g.; Sb, 0.2338 to 0.4187 g.; Current, 0.35 amp.; E. M. F., about 3 volts; Time, overnight.

Cc. HNO ₃	40	35	40	50
Cc. HF (48%).....	2	2	2	3
Gram Hg taken.....	0.4030	0.4030	0.2015	0.2015
Gram Hg found.....	0.4033	0.4026	0.2012	0.2013

The time required for the precipitation, as given in the foregoing tables, may seem unnecessarily long, and doubtless is. We found it convenient to start the runs in the evening and end them next morning. Probably all the mercury is down in six hours.

When tungstates and molybdates of the alkali metals are warmed with dilute nitric or sulfuric acids containing some hydrofluoric acid, clear and limpid solutions are obtained upon which an electric current has no reducing action. In comparison with solutions of stannic and antimonie acids containing hydrofluoric acid, the following facts, which have been established by careful experimental work, are interesting:

(1) A solution of stannic acid containing hydrofluoric acid is not reduced by the electric current, nor by warming with an excess of metallic zinc, nor by hydrogen sulfide.

(2) A solution of antimonie acid containing hydrofluoric acid is not reduced by the electric current, nor by warming with an excess of metallic zinc, but it is slightly reduced, although very sluggishly, by hydrogen sulfide, a small amount of antimony sulfide being precipitated.

(3) A solution of tungstic acid containing hydrofluoric acid is not reduced by the electric current, but it is reduced by metallic zinc. Hydrogen sulfide occasions no precipitation of tungstic sulfide.¹

(4) The behavior of a solution of molybdic acid containing hydrofluoric acid toward the current and metallic zinc is, in general, similar to that shown by a corresponding one of tungstic acid. Hydrogen sulfide, however, precipitates MoS₃ slowly from a hot hydrofluoric acid solution.¹

Separation of Copper from Tungsten.—A nitric acid solution of electrolytic copper was used. Found: 25 cc. = 0.2005 g. Cu (average of 5 well-agreeing determinations).

A solution of tungstic acid of convenient strength was prepared by dissolving 8.0001 g. of purified tungstic acid in a little caustic potash, filtering the solution and diluting the filtrate to a liter. The WO₃ present was determined according to the method recommended by Treadwell.² Found: 25 cc. = 0.1779 g. WO₃ (average of 3 well-agreeing determinations).

¹ In regard to this, as well as some of the foregoing reactions, see A. A. Noyes, "A System of Qualitative Analysis, Including Nearly All the Metallic Elements, Part II," *Tech. Quart.*, 17, 214 (1904); also McCay, *This Journal*, 31, 373 (1909).

² Treadwell, "Quantitative Analysis," 1908, p. 228.

Vol. 100 cc., containing 0.2005 g. copper, 0.1779 g. tungstic acid, 5 cc. conc. HNO_3 , and 5 cc. HF . E. M. F., about 3 volts; Current, 0.33 amp.; Time, overnight.

Gram Cu found (cor. for Pt)..... 0.2001 0.2003 0.2004 0.2006 0.2003 0.2001

The deposits were compact, adherent and usually salmon-pink in color. Occasionally they presented quite a burnished appearance. They always contained a little platinum, but never more than half a milligram. In the next series both the copper and the tungstic anhydride were determined. The quantities of copper, tungstic acid and of nitric and hydrofluoric acids used were the same as those just given. The current ran overnight.

Gram Cu found (cor. for Pt)..... 0.2003 0.2001 0.2007

Gram WO_3 found..... 0.1776 0.1771 0.1780

In each case the liquids and washings siphoned off from a copper deposit were evaporated in a platinum dish to dryness, and the tungstic anhydride was determined according to the method recommended by Treadwell.¹

Separation of Copper from Molybdenum.—The copper solution was the one we employed in the separation of the metal from tungstic acid. 25 cc. of the molybdic acid solution used in the first separations contained 0.3026 gram MoO_3 .²

Vol. of solution, nitric and hydrofluoric acids, as under separation of copper from tungsten. The current ran overnight.

0.2005 g. Cu and 0.3026 g. MoO_3 taken (0.4010 Cu in 7; 0.6052 MoO_3 in 6); E. M. F., 2.5 to 3 volts.

Current, ampere..... 0.33 0.50 0.50 0.33 0.33 0.33 0.33

Gram Cu (cor. for Pt)... 0.2006 0.2006 0.2006 0.2001 0.2004 0.1997 0.4012

All of the deposits were bright, and some of them of a burnished appearance. They were not in all cases distributed uniformly over the surface of the dish, but we noticed no tendency on the part of the metal to scale off, or separate out in spongy form. The results of some determinations of the molybdic anhydride in the liquids from which the copper had been deposited prove that the method is very satisfactory.

In all the separations of copper from molybdenum we detected platinum in the former metal. The amount, however, never exceeded half a milligram.

Separation of Copper from Tungsten and Molybdenum.—The solution electrolyzed contained in each case 0.1779 g. WO_3 , 0.3026 g. MoO_3 , 0.2004 g. Cu, the quantities of nitric and hydrofluoric acids above specified, and the volume amounted to about 100 cc. Current, 0.33 ampere; E. M. F., 2.3 to 2.6 volts; ran overnight.

¹ *Loc. cit.*

² The determinations were made according to the directions given by Treadwell. See his "Quantitative Analysis," 1908, p. 222.

Gram Cu found (cor. for Pt)..... 0.2002 0.2003 0.2001 0.2004 0.2006

In the determinations with rotating anodes which follow, the degree of dilution of the solutions, the acid concentrations, amounts of tungstic and molybdic acids present, etc., were the same as before.

0.2010 g. Cu taken: R. P. M. of anode, 550-650.

Current, amperes.....	4.00	1.75	1.00	1.75	1.75
E. M. F., volts.....	3.5	3.0	3.0	4.0	4.0
Time, min.....	65	70	60	60	60
Gram Cu found (cor. for Pt).....	0.2012	0.2010	0.2008	0.2009	0.4018

The separation of lead as lead peroxide from tungstic and molybdic acids in nitrohydrofluoric acid solution is complete, but the peroxide deposited, even after it is dried to constant weight at 200°, is decidedly too heavy. This fact has already been referred to. In Col. I of Table I are the results of the determinations of the lead in 25 cc. portions of a standard solution of pure lead nitrate containing 6.001 g. of the salt in a liter. In Col. II are the weights of the peroxide found. The deposits were obtained by adding 20 cc. conc. nitric acid to 25 cc. of the solution, diluting with water to 100 cc. and submitting the liquid to the action of the current. When a rotating electrode was employed precipitation was complete in an hour. When the precipitation was carried out in the ordinary way the current was allowed to act overnight. In Col. III are the values for lead peroxide obtained after dissolving¹ some of the deposits whose weights are given in Column II, in nitric acid and again electrolyzing the solutions under the same conditions, *but with the addition of 5 cc. of HF*. Col. V contains the weights of lead obtained by converting the two deposits whose weights are given at the end of Col. III into nitrate of lead, igniting it and weighing the oxide. In Col. IV we have the over-weights in milligrams, which are due to water and fluorine in some form, and in the last column but one the times during which the current acted in precipitating the peroxide whose weights are given at the end of Col. III.

TABLE I.

I.	II.				III.	IV.			V.
Gram.	Gram.	Amps.	Volts.	Time.	Gram.	Mg.	Time.		Gram.
0.0937	0.1082	4.0	3.5	1 hr.
0.0940	0.1085	0.5	2.0	Overnight	0.1097	1.2
0.0942	0.1087	0.5	2.0	Overnight
0.0940	0.1085	4.0	3.5	1 hr.
0.0940	0.1085	4.0	3.5	1 hr.	0.1095	1.0	Overnight	
0.0940	0.1085	4.0	3.5	1 hr.	0.1100	1.5	Overnight		0.0932
0.0942	0.1087	4.0	3.5	1 hr.	0.1100	1.5	Overnight		0.0938

Calculated: 25 cc. = 0.0938 g. Pb. Found: 25 cc. = 0.0940 g. (average of I) and 25 cc. = 0.0935 (average of V).

¹ 20 cc. conc. nitric acid are put in the dish, water is poured in until the deposit is covered, and the direction of the current is reversed.

The lead peroxide was deposited in a Classen dish roughened by means of a sand blast. Since this dish is made the anode, and a large surface is consequently exposed to the action of oxygen, which in the presence of hydrofluoric acid has a slight action on platinum, it may lose in weight during the electrolysis, and should, therefore, be reweighed after dissolving out the peroxide with dilute nitric acid containing 2-3 cc. of pure 3% hydrogen peroxide.

The Separation of Lead from Tungsten.—The lead solution was the one employed in making the immediately preceding determinations. The tungsten solution contained in 25 cc. 0.1812 g. WO_3 (average of 3 well-agreeing determinations).

The results of our work are embodied in Table II. In each case 0.0938 g. Pb, 0.1812 g. WO_3 , 20 cc. conc. HNO_3 and 5 cc. HF were present in a total volume of 100 cc. The weights of the PbO_2 deposited from nitrohydrofluoric acid solution are given in the first row, and the weights of the PbO_2 reprecipitated from nitric acid solution alone in the second. The third row contains the amounts of lead found, calculated from the weights as given in the second, and the fourth row the values for lead obtained by dissolving the deposits, whose weights are given in II and I (5, 6, 7), in a little nitric acid and pure 3% hydrogen peroxide, evaporating the solutions to dryness, igniting the residue and weighing the lead oxide.

TABLE II.

Current, 0.5 amp.; E. M. F., 2.5 volts; Time, overnight.

I, gram	0.1121	0.1127	0.1117	0.1125	0.1118	0.1125	0.1127
II, gram	0.1079	0.1088	0.1087	0.1085
III, gram	0.0934	0.0943	0.0942	0.0940
IV, gram	0.0935	0.0941	0.0941	0.0942	0.0941	0.0940

It will be observed that the weights of the deposits in the first row are from 3-4 mg. in excess of what they are in the second. The over-weights are, as has been already said, due partly at least to fluorine.

In the next series of determinations both lead and tungstic acid were estimated. In each case 25 cc. of the lead (0.0938 g. Pb) and of the tungstic acid solutions (0.1812 g. WO_3) were pipetted into a weighed platinum dish, 5 cc. of hydrofluoric and 20 cc. of concentrated nitric acids were added, the liquid was diluted to about 100 cc. and the current applied overnight (0.5 A. and at 2.5 V.). Since dilute nitrohydrofluoric acid attacks lead peroxide quite slowly, the liquid above the deposits was not siphoned off but poured off into a large ceresin beaker immediately after the current had been broken.¹ The peroxide was then washed as rapidly as possible with small amounts of water. After removing the hydrofluoric acid by evaporating the solution with conc. nitric acid in platinum,

¹ THIS JOURNAL, 36, 2380.

the tungstic anhydride was determined as before. The lead peroxide was dissolved and redeposited.

Gram Pb found.....	0.0937	0.0939	0.0948	0.0943
Gram WO_3 found.....	0.1797	0.1815	0.1806	0.1805

The Separation of Lead from Molybdenum.—The molybdic acid solutions used in the previous work were here employed, 0.3026 g. MoO_3 being present, and other conditions as in the preceding. The lead was determined as oxide or sulfate.

Gram PbO_2 found....	0.1106	0.1106	0.1103	0.1107	0.1115	0.1114
Gram Pb found.....	0.0933	0.0935	0.0933	0.0933	0.0934	0.0935

The fact that, in the separation of copper and mercury from tin, antimony, tungsten and molybdenum, small amounts of platinum are precipitated along with the former metals, is paralleled in these lead separations by the fact that the cathode gains steadily in weight. The deposit is undoubtedly platinum, for it is insoluble in all the ordinary solvents. Moreover, if such a discolored electrode be used in a copper or mercury determination it gradually brightens and sometimes the metal deposited will contain a milligram of platinum. The following are five successive gains of the cathode employed in the last series of separations:

0.0002; 0.0002; 0.0002; 0.0003; 0.0002 = 0.0011 g.

We also made some determinations of the molybdenum present in the liquid from which the lead had been removed. The liquid was not siphoned off but poured off into a large ceresin beaker the instant the current was broken. Calculated, 0.0939 g. Pb and 0.2245 g. MoO_3 .

Gram Pb found.....	0.0939	0.0941	0.0933
Gram MoO_3 found.....	0.2253	0.2244	0.2238

The lead was weighed as PbO_2 after solution and redeposition.

The Separation of Lead from Tungsten and Molybdenum.—The method of procedure, conditions, etc., will be evident from what has gone before. The lead was determined by converting the peroxide into the sulfate. The weights of the PbO_2 deposits, as well as the overweights, are given for the purpose of comparison.

0.0939 g. Pb; 0.1812 g. WO_3 ; 0.3026 g. MoO_3 taken.

Gram Pb found.....	0.0943	0.0939	0.0932	0.0939	0.0946
Gram PbO_2 found.....	0.1113	0.1121	0.1131	0.1116	0.1116
Milligrams overweight.....	2.9	3.7	4.7	3.2	3.2

It will be noted that when tungstic and molybdic acids are present, the overweights are considerably greater than they are when the peroxide is precipitated from nitrohydrofluoric acid solutions alone. The overweights are, as we have already stated, due partly, possibly almost wholly, to fluorine in some form. Peroxide of lead is decomposed with difficulty by concentrated sulfuric acid, but on long heating to a point just below that at which the acid begins to fume the transformation into

the sulfate is almost complete. The residue is never white, but of a pink color. In testing for fluorine we have made use of a device which dispenses with waxed or paraffined watch glasses. The peroxide which has been deposited in a smooth platinum dish, from which most of it can generally be easily removed, is, after a thorough washing, and drying at 200° , ground to an impalpable powder in a small agate mortar, and a convenient amount is weighed out in an ordinary platinum crucible. A little concentrated sulfuric acid is added and the mass well stirred with a small platinum spatula. A platinum Gooch, with a mouth of which the diameter is somewhat less than that of the other crucible, is *inverted* and forced gently into the lower crucible until it remains in place and upright. A fairly tight joint between the two is thus obtained. Over the holes in the Gooch is placed a small glass cover, such as is employed in microscopical work, and the bottom of the lower crucible is heated with a tiny flame to a temperature barely high enough to make the sulfuric acid fume. At the end of half an hour the cover is removed, washed and dried. All the samples of lead peroxide deposited from nitrohydrofluoric acid solution which we examined in this way (we used from 0.1–0.3 g. for a test) gave us fine reactions for fluorine. In most cases perfect patterns of the perforated surface on which the glass cover rests were obtained. It is hardly necessary to state that we convinced ourselves by numerous blank experiments that the acid alone, as well as mixed with peroxide free from fluorine, had no action on the glass. The test is exceedingly delicate, for by means of it we have had no trouble in detecting 0.0001 g. of fluorine. If a platinum Gooch is not at hand, cover the crucible containing the mixture of fluoride and concentrated sulfuric acid with a piece of platinum foil, in which a number of small holes have been pierced with a needle, press it down firmly and place the glass slip over the holes.¹

Separation of Mercury from Tungsten.—The following determinations of mercury in the presence of tungstic acid show that the method is very satisfactory. Everything worked well from start to finish, and the appearance of the mercury deposits left nothing to be desired. The solution in each case, when ready for electrolysis, amounted to from 100–110 cc., and contained 0.1779 g. WO_3 , 5 cc. conc. HNO_3 , and 5 cc. 48% HF. The current ran overnight.

Current, ampere.....	0.5	0.5	0.5	0.5	0.3	0.3
E. M. F., volts.....	4.0	3.0	2.8	3.0	3.5	2.5
Gram Hg taken.....	0.2006	0.2006	0.2006	0.4012	0.4012	0.4012
Mg. Pt found.....	0.3	0.3	0.1	0.5	0.3	0.1
Gram Hg found (cor.).....	0.2006	0.2001	0.2001	0.4013	0.4020	0.4021

¹ This modification of the usual method for testing for fluorine is not mentioned in the treatises of Fresenius, Classen and Treadwell. We had supposed that the device was new, but find that it was suggested by F. von Kobell in 1864. See *J. prakt. Chem.*, 92, 389 (1864).

Separation of Mercury from Molybdenum.—Our first results were unsatisfactory. The mercury deposits were gray, spotted here and there with black specks, and from 2–6 mg. higher than they should have been. The solutions too, which were originally colorless, became in the course of time faintly greenish yellow, and the platinum dish employed was attacked to an unusual degree. The losses in weight of the dish were very irregular, varying from 2–7 mg. We have found, however, that by employing a relatively low electromotive force (less than 2 volts) the separation is complete and satisfactory, the only irregularity being the loss in weight suffered by the dish when the mercury deposits were dissolved in nitric acid. The weight of the anode remains practically constant, and this was our experience in separating silver from tin and antimony, where a small electromotive force was employed.

The determinations of mercury which follow were made with a solution containing 0.2083 g. mercury per 25 cc. Barring the low electromotive force the conditions were about the same as those generally observed.

0.2032 to 0.2222 g. MoO_3 taken; Current, 0.1 amp.; E. M. F., 1.4 to 1.6 volts; Time, overnight.

Gram Hg found.....	0.2079	0.2077	0.2078	0.2080	0.2083	0.2086	0.2086
Mg. anode loss.....	0.3	0.1	0.1	0.3	0.1	0.0	0.0

Cold nitric acid of 1.26 sp. gr. dissolves quite readily the bright mercury deposits, but a *gray film* always remains on the dish, which disappears slowly but completely on warming the acid. It dissolves more rapidly in concentrated nitric acid. The cold dilute nitric acid solution contains most of the mercury and a small amount of platinum, while the solution of the gray film, in addition to the rest of the mercury, contains a comparatively large amount of platinum. When such a solution, after dialysis, is evaporated to dryness in a porcelain crucible and the residue strongly ignited, a small amount of a black substance remains which dissolves only in aqua regia, and gives with stannous chloride fine reactions for platinum. The loss in weight of the dish amounted to 2.5 mg., which is the average of a number of determinations. That the dissolved platinum can be recovered will be evident from the following results. They correspond to the determinations of mercury given in the preceding tabulation.

Dish lost, mg.....	1.2	0.9	2.4	4.5	1.9	1.8	3.4	1.5
Pt in 1 : 1 HNO_3	0.6	0.6	...
Pt in conc. HNO_3	1.3	1.2	2.4	4.5	2.6	1.3	3.2	1.5

Just what role is here played by the molybdenum we are unable to say. It certainly accelerates the rate at which the dish is attacked, and conditions the formation of the gray film. The usual loss in weight of a dish when mercury is deposited from its dilute nitric acid solution alone is never over 0.5 mg. The molybdic acid employed had, as said, been

digested for a long time with boiling conc. nitric acid. It dissolved in ammonium hydroxide without leaving any residue, and, tested according to the directions given by Merck,¹ gave no reactions for heavy metals.

Separation of Mercury from Tin, Antimony, Tungsten and Molybdenum.—Very satisfactory results were obtained by one of us (F.) in determining the amount of mercury present in a solution of unknown concentration.

Vol. soln., 100–110 cc. containing approx. 0.2 g. Sn, 0.1 to 0.25 g. Sb, 0.2 g. WO_3 and 0.2 to 0.26 g. MoO_3 ; Current, 0.1 amp.; E. M. F., 1.4–1.5 v.; Time, overnight.

(Double quantities of Hg were taken in last two determinations.)

Dish lost, mg.....	3.2	1.5	1.5	2.0	1.8
Pt found, mg.....	3.1	1.9	1.2	2.4	2.3
Gram Hg found.....	0.1565	0.1570	0.1558	0.3137	0.3124

Average for 25 cc. = 0.1565 g. Should be 0.1565. Weight of anode remained constant.

Separation of Silver from Tin, Antimony, Tungsten and Molybdenum.—The conditions here observed were very similar to those described in connection with the separation of silver from tin and antimony, but the solutions were held in a ceresin beaker and the metal was deposited on a Winkler gauze electrode.

Vol. of soln., 250 cc. containing 0.020 g. Ag, 0 to 0.2 g. Sn, 0 to 0.1 g. Sb, 0 to 0.14 g. WO_3 and 0.1 to 0.22 g. MoO_3 ; Current, 0.05 amp.; E. M. F., 1 volt; Time, overnight.

Gram Ag found.....	0.0198	0.0197	0.0200	0.0199	0.0198	0.0200
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Wt. of anode constant as result of low E. M. F. No correction for Pt.

Silver can be separated from all the above-mentioned metals in one hour by using a rotating anode.

Vol. of soln., 250 cc. containing approx. 0.2 g. Sb, Sn, WO_3 , and MoO_3 each. Current, 0.5–0.75 amp.; E. M. F., 2.2 to 2.75 v.; R. P. M., 500–550; Time, 40 minutes.

Gram Ag taken.....	0.0375	0.0375	0.0375	0.0200	0.0200
Gram Ag found.....	0.0380	0.0379	0.0373	0.0197	0.0202

The silver deposits were light gray, compact, and firmly adherent. The anode used was a long platinum-iridium spatula, and was not attacked during the series of determinations, as its weight was found to remain constant. Hence no corrections were necessary.

Additional Facts on the Separation of Copper from Other Metals by the HF Method.—Copper can be separated from tin, antimony, tungsten and molybdenum, when all of these metals are present in nitrohydrofluoric acid solution, observing the usual conditions of voltage, dilution, etc. Further, if a voltage of less than 2.0 be used, copper can be quantitatively separated from arsenic, or arsenic and the four elements mentioned.

These facts will be evident from the results given in the following tabulation. The procedure will be obvious from preceding descriptions.

¹ "Chemical Reagents," Merck & Co., 1914.

0.2010 g. Cu taken and 0 to 0.2 g. Sn, 0 to 0.2 g. Sb, 0 to 0.2 g. WO_3 , 0 to 0.22 g. MoO_3 ,
0 to 0.5 g. KH_2AsO_4 .

Current, ampere.....	0.25	0.2	0.1	0.1	0.1	0.05	0.1	0.1
E. M. F., volts.....	2.4	2.4	1.4	1.4	1.4	1.3	1.7	1.7
Gram Cu found.....	0.2013	0.2012	0.2015	0.2009	0.2011	0.2011	0.2011	0.2010

The first two results given have the copper value corrected for platinum present. In the last six determinations no correction is made, for although in some cases a faint qualitative reaction for platinum was obtained, in no case was there a weighable amount deposited with the copper.

As an example of the immediate practical application of the HF method for separating copper from W, Mo, etc., we offer the following determinations of the copper in an alloy (No. 117) prepared by S. W. Parr.¹ Mr. S. F. Cox was kind enough to furnish us with a sample of the alloy. According to the analysis of Rowland and Braley, the alloy contains 6.42% Cu.

We find: 6.37; 6.59; 6.44; average, 6.46.

A number of interesting theoretical matters have come up in connection with the use of hydrofluoric acid in electrochemical analysis. Some of these are being investigated.

PRINCETON, N. J.

NOTE.

Note on a Convenient Dip Electrode.—In the determination of the conductivity value² and of the volumetric lead number³ of maple syrups, conductivity cells with very rigid electrodes are required, so that the distance between the electrodes may not be altered in stirring the somewhat viscous diluted syrup. The cell recommended by Snell⁴ is unsuitable for the volumetric lead determination, inasmuch as the precipitate settles upon the horizontal electrodes. Its unprotected electrodes are also subject to accidental displacement.

The small dip electrode⁵ used in beginning the work on the determination of the volumetric lead number of maple syrup, also proved to be unsatisfactory, since the electrodes were much too small and were also subject to displacement when the diluted syrups were stirred.

The writer overcame these disadvantages by designing the electrode shown in the illustration. It consists of a hard glass cylinder 6.5 cm. high by 3.7 cm. in diameter open at both ends. One end is fitted with a vulcanite cap, B, and is fastened to the cylinder by means of set screws.

¹ "An Acid-Resisting Alloy to Replace Platinum in the Construction of a Bomb Calorimeter," *THIS JOURNAL*, 37, 2515 (1915).

² Snell, *J. Ind. Eng. Chem.*, 5, 740 (1913).

³ Snell, MacFarlane and Van Zoeren, *Ibid.*, 8, 241 (1916).

⁴ *Loc. cit.*

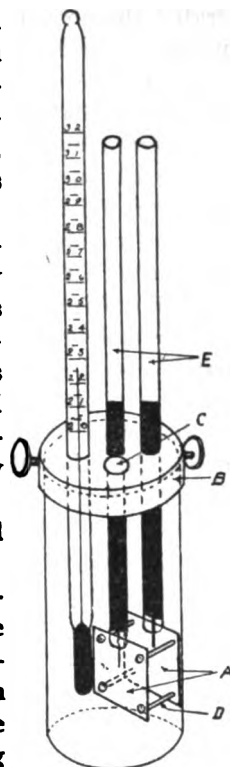
⁵ Snell, *J. Ind. Eng. Chem.*, 8, 144 (1916).

A thermometer and two glass tubes pass through the cap. The hole C allows the air to escape when the electrode is immersed into a solution. The platinum connecting wires, which are welded to the electrodes, are protected by being sealed in the tubes E, in which mercury is placed to connect the electrodes with the bridge leads.

The electrodes A are of No. 30 B & S gauge platinum foil 2 x 2 cm. squares set one cm. apart. They are firmly fastened together by means of four glass pins as shown (D). The pins have small enlargements two millimeters from each end, which serve as collars and prevent the electrodes from being crowded together. The ends of the pins pass through the electrodes and are clinched. In this way they are firmly held in place.

An ordinary 100 cc. hard glass beaker may be used to complete the cell.

The electrode has proven so convenient and trustworthy, that the writer desires to bring it to the notice of his fellow chemists and others who may perhaps find use for it, since it can well be adopted in other lines of work on conductivity. It can easily be constructed by any one having a little skill in making apparatus.



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CORRECTION.

In the February JOURNAL, page 361, line 25 should read " $\gamma = 10 + \text{no. of centimeters,}$ " instead of " $\gamma = 1 + \text{no. of centimeters.}$ "

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE REARRANGEMENT OF ISO INTO TERTIARY BUTYL BROMIDE.

BY A. MICHAEL, E. SCHARF AND E. VOIGT.

Received January 4, 1916.

The structural rearrangement of an alkyl halide was first proven by Eltekow,¹ who found that isobutyl and isoamyl bromides are partially converted, by heating in a sealed tube to 230°, into the corresponding tertiary derivatives. Eltekow, and also Aronstein,² who later demon-

¹ Ber., 6, 1258 (1873); 8, 1244 (1875).

² Rec. trav. chim., 1, 1346 (1882).

strated the conversion of primary into secondary propyl bromide, were unable to reverse the reaction, although in no case could a complete isomerization be realized. It was only in 1907 that Faworsky¹ succeeded in proving that secondary and tertiary alkyl halides could be partially reconverted by heat into the primary products and thus explained why these reactions are limited. Michael and Leupold² found that the isomerization of isobutyl bromide begins and proceeds very slowly at 92–95°, but rapidly at 180°, and that it is much accelerated by increasing the surface of the liquid in proportion to its mass. A condition of equilibrium is reached with the formation of about 74% of tertiary from iso and about 26% of iso from tertiary butyl bromide. The change of the tertiary bromide begins, however, at a much higher temperature than its isomer and proceeds slowly even at 180°. It is evident that the relations between the velocities of isomerization do not harmonize with the usual assumption that they determine the limit of such a reaction; thus, a mixture of 74% iso and 26% tertiary butyl bromide, *i. e.*, in the proportion representing the equilibrium of the bromides in the heat, undergoes no change at 140°, although at that temperature the iso compound alone rapidly isomerizes, while the tertiary bromide alone remains practically unchanged.

The investigation was continued by Michael and Zeidler,³ who showed that the isomerization of isobutyl bromide depends to a remarkable degree on the purity of the compound, very small amounts of certain substances being capable of retarding it almost completely at temperatures at which the pure product changes rapidly. Several of their preparations could be distilled only a limited number of times without undergoing some decomposition and isomerization; indeed, with two of them a small amount of tertiary bromide was formed on standing for several weeks in a brown desiccator at room temperature. The repeated fractionation of their isobutyl bromide removed some unknown impurities, whose presence greatly retarded the isomerization. In the present paper, we have endeavored to ascertain the conditions for preparing a purer isobutyl bromide; to examine the properties of such a product; and to study its rearrangement into tertiary butyl bromide quantitatively. Unfortunately, the purer substance shows such an extraordinary instability and sensitivity to the influence of positive and negative catalytes that we have not succeeded in obtaining better, *i. e.*, more constant, quantitative results than in the previous investigations. The purest isobutyl bromide was obtained by heating isobutyl alcohol with hydrobromic acid in sealed tubes to 65°; it is essential, however,

¹ *Ann.*, 354, 325 (1907).

² *Ibid.*, 379, 263 (1910).

³ *Ibid.*, 393, 81 (1912).

to use the alcohol and acid in a very pure condition. For this purpose, Merck's best alcohol was fractionated until a practically constant boiling product was obtained, which was then converted into the boric ester, the latter fractionated *in vacuo* until constant boiling, and then saponified. The hydrobromic acid was prepared catalytically, using pure bromine and electrolytic hydrogen.

To what an astonishing degree the properties of isobutyl bromide are influenced by the presence of minute, intangible impurities, is shown by the following comparison of some of the properties of our purest product with those noticed by previous observers. Isobutyl bromide has been always considered a stable substance that could be distilled an unlimited number of times without undergoing any decomposition. In the first seven preparations of the bromide we endeavored each time to increase the quality of the product by changes in the method, and added purity of the chemicals, and we noticed that the stability of the bromide decreased in direct proportion to its purity. With the eighth preparation we obtained it in a condition that any further slight changes we made did not perceptibly influence its properties. Preparation VI could be distilled twice under ordinary pressure without forming hydrobromic acid, VII only once and VIII, and the later products, not at all. Equally sensitive to the purity is the capacity of the bromide to isomerize. Michael and Leupold¹ heated their carefully prepared product at its boiling point for 50 hours without being able to prove the formation of tertiary bromide. Our purest products could not be distilled without some of that substance being formed; indeed, this change took place slowly when it was kept in a brown desiccator at room temperature. The same observers were able to study the rearrangement in sealed bulbs at temperatures up to 235° and only at about 260° did they notice a decided decomposition. Our best products often became brown through decomposition at 108° and at 142° they could only be heated a short time; at 260° the liquid flashed with total decomposition. Michael and Zeidler² succeeded in preparing a bromide from a comparatively inert product by repeated fractionation that practically reached the limit of rearrangement after one hour at 142°, but our purest products were equally, or more sensitive, after one distillation in a vacuum; indeed, in our last preparations the crude, undistilled products were extremely reactive.

Not alone in the liquid, but, also, in a gaseous state, is our purest isobutyl bromide much more susceptible to rearrangement than the products hitherto examined. Thus, Michael and Leupold³ were unable to detect

¹ *Ann.*, 379, 305 (1910).

² *Ibid.*, 393, 104 (1912).

³ *Ibid.*, 379, 301 (1910).

any change at 142° and, at 184° , only 2.7% of tertiary derivative was formed in $2\frac{1}{2}$ hours; our Preparation VII showed about the same amount after 3 hours at 100° and, after $\frac{1}{2}$ hour at 184° , it gave 53.5% tertiary butyl bromide. It seemed of interest, therefore, to determine the vapor density of this bromide. Michael and Leupold could not prove dissociation at 184° , although tertiary butyl bromide at that temperature broke down to the extent of 36%. At 142° , in a Meyer apparatus, we were unable to prove dissociation with certainty,¹ at 184° an amount of gas was obtained almost at once that corresponded to the normal vapor density, then for 20 minutes a further evolution of gas gradually occurred until about 50% of the bromide was dissociated. This result makes the nature of the rearrangement in gaseous condition at 184° uncertain, since, if isobutyl bromide dissociates at that temperature, evidently part of the change may proceed in this way. On the other hand, the reaction undoubtedly takes place intramolecularly in gaseous condition, as we observed the formation of tertiary bromide at 100° , while dissociation of isobutyl bromide could not be proven at 142° .

We also examined the behavior of our purest bromide in gaseous state towards asbestos, glasswool, sand and other substances that, according to Konowalow,² dissociate the vapor of such organic halides catalytically. In agreement with the results of Michael and Leupold,³ we found at a temperature (142°) where the vapor density of the bromide is normal, that these substances are inert, as when introduced into the gas they caused no change in its volume. Even the addition of powdered "Geraeteglas," which, as we shall presently describe, increases the rearrangement of the bromide in a liquid condition very considerably, had no effect on it in a gaseous state. While we were unable to find a substance that acts as a positive catalyte on the dissociation of gaseous isobutyl bromide, it follows from our results that the phenomenon is dependent to an extraordinary degree on the purity of the compound, *i. e.*, on the removal of most minute traces of a substance or substances that show a negative catalytic influence. This result should be given full consideration in future investigations of this and similar compounds. We confirmed, too, the observations of Michael and Zeidler⁴ on the action of negative catalytes on the liquid bromide with our purest product; such substances, as diisobutene, iso and tertiary butyl alcohol, when

¹ The analysis of the contents of the apparatus after heating showed indeed the presence of about 5% tertiary bromide, which according to Roozeboom's (*Ber.*, 14, 2396 (1881)) determinations would cause 0.5% dissociation, but the tertiary product may have been formed by direct isomerization.

² *Ber.*, 18, 2808 (1885).

³ *Ann.*, 379, 311 (1910).

⁴ *Ibid.*, 393, 83 (1912).

added in a small proportion, greatly decrease not only the rearrangement but the limit of the reaction.

Ground surfaces, whether of glass or of quartz, also act as negative catalytes on the rearrangement of the bromide in the liquid state. This is very noticeable when the experiments are conducted in small Hofmann bottles with ground-in stoppers and it is remarkable that the isomerization is more retarded in quartz than in glass vessels. Thus the mean value, for 1 hour at 108° , in glass bottles was 5.2%, and in those of quartz 1.9%, of tertiary bromide. In agreement with the conclusion that the ground surfaces act catalytically on the liquid bromide is the fact that in the presence of an extremely small bubble of air in the bottles the isomerization is considerably less retarded, as under the same conditions of heating, the mean values rose to 11.7% in glass and 3.8% in quartz bottles. This conclusion was further confirmed by carrying out the experiments in a quartz bottle with a long capillary neck, and with bulb only filled to one-half, and in a completely filled Hofmann bottle of the same material, when, under like conditions of heating, the mean value in the long bottle was 11.7% and in the short one 3.8% of tertiary bromide. Although the bromide in these experiments remained colorless after heating, it seems not improbable that the retardation of isomerization is due to the formation of by-products in so minute an amount that the change of coloration is not perceptible to the eye.

According to Michael and Leupold the limit of the rearrangement of iso into tertiary butyl bromide is reached when about 74% of the latter product is formed, while Michael and Zeidler, with a purer product, found it to be about 76%. With our purest isobutyl bromide the results were less concordant. Thus, with Preparation VII, we obtained 81.6% tertiary product after heating 3 hours, and 81.2% after 6 hours, at 142° , while VIII gave 75.5 and 69.1% after $1\frac{1}{2}$ and 3 hours at the same temperature and 67.6, 73.2 and 67.0% after $\frac{1}{4}$, $\frac{1}{2}$ and 1 hour at 184° . At a lower temperature the limit was considerably less; at 108° only 16.4, 20.2 and 19.8% of tertiary product was formed after heating for $\frac{1}{2}$, 2 and 4 hours. These results are in accordance with the tendency of very pure isobutyl bromide to decompose readily, with the formation of unknown by-products that materially interfere with the rearrangement.

The conversion of a primary alkyl bromide into an isomer through the use of a chemical reagent was first noticed by Kekulé and Schroetter,¹ who found that normal propyl bromide is largely converted into the secondary product by heating with aluminium bromide. Gustavson² examined the reaction more carefully and found that it is complicated by the formation of a double compound of the salt with unsaturated

¹ *Ber.*, 12, 2280 (1879).

² *Ibid.*, 16, 958 (1883).

hydrocarbons formed in the process and that this double compound is also capable of converting the normal into the secondary bromide. He also noticed that the rearrangement is dependent on the temperature and on the amount of the salt. In the same manner trimethylene bromide has been converted into propylene bromide.¹ It seems probable that these changes are indirect, that is, the aluminium salt enters into chemical union with the bromide, and we thought it of interest to examine whether our reactive product is subject to direct, positive, catalytic influences.

It is remarkable that Jena "Geraete" glass contains such a positive catalyte, as rearrangement in it takes place almost three times as fast as in Jena hard, or ordinary soft glass. Thus, in "Geraete" glass after $\frac{1}{2}$ hour at 108° about 44% of tertiary derivative was formed but only 16.9% in hard glass. We were unable to determine whether the glass itself acts directly as the catalyte, or through the formation of another compound by the chemical action of the bromide. If the latter suggestion should be correct the amount of new substance thus formed must be practically infinitesimal in quantity, for we boiled powdered "Geraete" glass a long time with isobutyl bromide and were unable to detect a solid residue in evaporation of the liquid.

The main difference between "Geraete" and the other varieties of glass used in our experiments is that it contains a considerable percentage of zinc oxide. It may be supposed, therefore, that zinc bromide formed in the action of the bromide on the glass is the active catalyte in the conversion. Indeed, this salt acts in a most minute amount as an extremely powerful positive catalyte. Thus, the presence of about 0.0001% of the salt almost doubled the rearrangement, while its presence in somewhat greater proportion (0.0004%) only increased the velocity of the reaction about 25% and caused the formation of colored by-products in small amounts and in presence of an appreciable amount the bromide after heating was dark colored and contained no tertiary product. The activity of zinc bromide in such an infinitesimal amount led us to examine whether so powerful a reagent as hydrobromic acid would extract zinc from "Geraete" glass, but we were unable to detect the presence of the metal in the acid, although the substances were digested for some hours. It is remarkable that the vessels of "Geraete" glass are less active on second use but they then show no change on further employment.

Mercuric chloride also acts as a strong positive catalyte. This salt is somewhat soluble in the bromide and solutions containing as little as 0.02% give high values of tertiary product on heating a short time at 56° . Another positive catalyte is hydrochloric acid; a solution of bromide with 0.3% acid contained 3% of tertiary bromide, after standing at room

¹ Gustavson, *J. prakt. Chem.*, [2] 36, 303 (1887).

temperature for 3 days, and the results obtained in heating such a solution showed a direct proportionality between time and percentage of tertiary bromide. On the other hand, calcium bromide and aluminium oxide are inert, and the addition of a trace of water to the bromide showed no appreciable influence at a low temperature.

The extreme susceptibility of the bromide to catalytic influences suggested that even air may play a role in the rearrangement. We found that isobutyl bromide is able to absorb a small amount of air, which may be easily shown by heating a sealed bulb with a long capillary tube and filled with bromide to within 10–15 mm. of the narrow end, when the liquid soon completely fills the vessel. An examination of the contents of the capillary tube and the bulb separately for tertiary bromide showed that the narrow part, which evidently contained a larger percentage of dissolved air, gave a somewhat greater proportion of the reaction product. The difference increased when the surface exposed to air was increased, as we were able to show by modifying the experiment; a second bulb was blown midway in the capillary of the container, which was filled with bromide until the upper bulb was half full and the experiment completed as before. These results appear to explain the fact noticed by Michael and Leupold¹ that the increase of surface in proportion to the mass of bromide increases the velocity of rearrangement. It seems probable that there is no influence of the surface *per se* on the rearrangement and that the larger velocity in wide than in narrow tubes in the experiments of Michael and Zeidler was due to a greater absorption of air, since the relation between surface and mass of the bromide was thereby increased. One may, therefore, refer to the influence of surface when the rearrangement is performed in the presence of air and to obtain comparable results under such conditions the mass of bromide and exposed surface should be the same in the experiments.

The above conclusion on the action of air is confirmed by the results obtained in heating the bromide in a homogeneous, liquid phase and in presence of a vacuum, although the results are less concordant among themselves, which is probably due to the experimental difficulties, than in the preceding experiments. For this purpose the bromide was first freed from dissolved air and, in one set of experiments, the bulbs with capillary ends were filled so that the expansion of the liquid on heating caused it to occupy the vacuum over it, while, in the second series, a vacuum still remained over the hot bromide. No difference in the mean values of tertiary bromide formed was found in these experiments, but in both series the amount was less than when the reaction proceeded under comparable conditions in the presence of air.

The results just described have a bearing on the question, whether

¹ *Ann.*, 379, 309 (1910).

the rearrangement of isobutyl bromide is subject to the influence of the free space over the liquid. Eltekow¹ heated the same amount of bromide in tubes of equal diameter but unequal lengths and concluded that the velocity of the reaction increases with the free space above the liquid. Michael and Leupold² repeated the experiment with iso, and also with tertiary, butyl bromide at temperatures between 140° and 235°, employing a more exact method than Eltekow. They concluded that the free space exercised little or no influence on the reaction. Later, Michael and Zeidler³ made similar experiments with isoamyl bromide and found that the presence of much free space increased the rearrangement from 0.6 to 2.0%. It obviously follows from the fact that absorbed air acts as a weak, positive catalyte, that the amount of the air may under certain conditions affect the extent of the rearrangement, but not necessarily, since the air present may suffice to saturate the bromide under the conditions of the experiment, in which case the excess should not exert a further influence.

The results, too, permit, in our opinion, a definite conclusion in regard to the mechanism of the rearrangement of iso into tertiary butyl bromide. Eltekow⁴ concluded from the increase of reactivity with free space over the liquid that the reaction occurs mainly in the gaseous bromide, *i. e.*, through dissociation into isobutene and hydrobromic acid and subsequent addition. Later⁵ when he found that the rearrangement proceeds at a temperature lower than that of the dissociation, he concluded that the isomerization takes place directly through intramolecular shifting of the atoms. This interpretation is supported by the results of Michael and Leupold,⁶ who gave the view a consistent theoretical basis, while Aronstein,⁷ Faworsky⁸ and Brunel⁹ assume that the reaction proceeds through dissociation. The latter view represents the conservatism that has been almost invariably shown in the development of chemical theory; at first the dissociation theory was fought with a determined opposition; then, after its general adoption, an equally determined opposition is shown to other views that stand better in harmony with the observed results. Since isobutyl bromide has a greater content of free *chemical* energy than the tertiary isomer, there must exist a tendency in it to isomerize and it would be an unstable compound under ordinary conditions, if its free

¹ *Ber.*, 8, 1247 (1875).

² *Ann.*, 379, 265 (1910).

³ *Ibid.*, 385, 292 (1912).

⁴ *Ber.*, 8, 1244 (1875).

⁵ Dissertation (1884); see Faworsky, *Ann.*, 354, 326, 333 (1907).

⁶ *Ann.*, 379, 264 (1910).

⁷ *Rec. trav. chim.*, 1, 134 (1882).

⁸ *Ann.*, 354, 325 (1907).

⁹ *Ibid.*, 384, 245 (1911).

chemical energy could overcome the chemical hindrance to the change. This chemical hindrance is represented by the affinity of bromine and the single hydrogen of the methine group to the other atoms in the molecule, primarily, however, to the carbons to which they are directly joined. With the rise of temperature this hindrance decreases while the substance is increasing in its free energy and, at a certain point, the value of the equation chemical affinity plus free *chemical* energy divided by chemical hindrance becomes positive. At this point an intramolecular rearrangement will occur, because by so doing the maximum increase of entropy with minimum expenditure of energy will be realized. In the fact that in laboratory experiments rearrangement and dissociation are sometimes concomitant lies no proof that the isomerized molecule has been formed through the latter process; indeed, it is more likely that we have unnecessarily added so much energy to the system that the isomerized product has been decomposed.

To reconcile the fact that the temperature at which the rearrangement of isobutyl bromide occurs is much lower than that at which dissociation takes place, Faworsky¹ refers to the researches of Menschutkin and Konowalow² and Konowalow,³ who found that many substances, such as asbestos or powdered glass, may lower very considerably the temperature of dissociation of similar products in a gaseous condition; also, to those of Konowalow⁴ and Zelinsky and Zelikow,⁵ where, in the presence of free acid, certain esters which are otherwise stable decompose on distillation. The experiments of Menschutkin and Konowalow were repeated by V. Meyer and Pond,⁶ who were unable to confirm their results, then Michael and Leupold⁷ failed to notice catalytic influence of such substances on the vapor of iso and tertiary butyl bromides and, finally, we were equally unsuccessful with our purest isobutyl bromide. We found, indeed, that hydrochloric acid acts as a positive catalyte on the isomerization of liquid isobutyl bromide, but in the dissociation of that compound along with the similar hydrobromic acid an unsaturated hydrocarbon is formed and such a substance retards the reaction very considerably, indeed prevents it entirely when present in 2 or 3%. Brunel⁸ heated isobutyl bromide to a very high temperature and concluded that catalytic influences entered into the reaction under these conditions and also in the experiments of Michael and Leupold with liquid bromide. However,

¹ *Ann.*, 354, 333 (1907).

² *Ber.*, 17, 1360 (1884).

³ *Ibid.*, 18, 2808 (1885).

⁴ *Z. physik Chem.*, 1, 63 (1887); 2, 6 (1888).

⁵ *Ber.*, 37, 1374 (1904).

⁶ *Ibid.*, 18, 1623 (1885).

⁷ *Ann.*, 379, 300-304 (1910).

⁸ *Ibid.*, 384, 245 (1911).

his results are not only inconclusive, but the conditions of the experiments permitted no safe inference in regard to the nature of the rearrangement even in the gaseous phase,¹ the more so as we now know that the temperature of dissociation depends on the purity of the bromide.

The facts revealed in this investigation stand in such a direct opposition to explanation of the isomerization proceeding by dissociation that the view is now untenable. This conclusion is inevitable when we consider that the stability of isobutyl bromide at ordinary temperature depends on the presence of an anticatalyte, and that in a pure state it slowly isomerizes, while no direct evidence of dissociation could be proven in gaseous condition at 142°; then, that the process occurs with equal facility in the liquid as it does in the liquid-gaseous phase, and, finally, that the addition of certain catalytes in infinitesimal amounts to the liquid bromide causes an enormous acceleration of the change at low temperatures, whereas no catalyte has been found that influences it in a gaseous condition.

Some of these relations are difficult to explain. Thus, it seemed probable that isomerization would take place more readily in gaseous than in liquid bromide, as the gaseous molecule appears to have the larger content of energy; also, that catalytic influence would then come readily into play. An explanation may be found that the chemical change in the liquid state takes place not in the separate molecule, but in an aggregation of them, the so-called "polymolecule,"² whose total energy may be greater than that of the gaseous molecule, and which disappears when the bromide passes into the gaseous condition. This, too, may explain the action of positive catalytes on liquid and not on gaseous bromide, the catalytes uniting with the "polymolecules" to form larger complexes with still more energy.³ We have shown in this research that the purest isobutyl bromide we could prepare is not a stable body, even at ordinary temperature, and that it differs so much in many of its properties from those of a product usually considered chemically pure, that it almost seems like a different compound. To what extent do the marvelous relations between purity, properties and catalytic forces, that are so manifest in isobutyl bromide, appear in other substances? This is a new question which science can only answer by laborious investigation, but it certainly seems not improbable that it is not an isolated case and that there are other compounds, whose existence and properties under ordinary conditions depend on the play of obscure catalytic forces.

¹ Michael and Zeidler, *Ann.*, 393, 89 (1912).

² Kekulé, *Ibid.*, 106, 141 (1858); Michael, *Ber.*, 34, 4028 (1901); 39, 2140, 2570 (1906); *THIS JOURNAL*, 32, 991 (1910).

³ Michael, *Am. Chem. J.*, 39, 4 (1908).

EXPERIMENTAL PART.

Preparation of Isobutyl Bromide.

According to Michael and Zeidler,¹ the best method of preparation consists in saturating at 0° a mixture of equal parts of isobutyl alcohol and constant boiling hydrobromic acid with gaseous hydrobromic acid, and heating the mixture in a sealed tube to 75–80°. The bromide obtained in this way was decidedly more sensitive to rearrangement than that prepared by any other method and a very reactive product was obtained from it by repeated fractionation. By very careful purification of all the products used in the reaction, and changes in the manipulation, we succeeded in improving the quality of isobutyl bromide made by this method to such an extent that the crude substance showed great reactivity.

The purest isobutyl alcohol obtainable was fractionated three times, using a long Hempel column; from 1 kilo about 400 g. of a product were obtained, which boiled constant within 0.15°. The isobutyl alcohol of commerce often contains traces of a basic substance, which cannot be removed by distillation and even passes over into the boric ester made from it. The alcohol purified by distillation was, therefore, extracted repeatedly with small amounts of dilute sulfuric acid, then several times with water and dried, first over fused potassium carbonate, then over lime. This was heated 6 hours at 160–175° in an autoclave with 1/4 of its weight of pure boric anhydride.² Isobutyl boric ester cannot be distilled under ordinary pressure without some decomposition and the residue left after distilling off the excess of alcohol was, therefore, fractionated two or three times *in vacuo*. In order to indicate smaller changes in the pressure during the fractionation than is possible with the usual mercury manometer, we used in connection with that instrument, one filled with nitrobenzene. The pure ester was then saponified by boiling a short time with aqueous alkali, in a flask connected with a return cooler, the alcoholic layer separated, extracted once with a little water and then dried over freshly heated lime. This product, which undoubtedly still contained a trace of water, boiled constant at 108.0° under 767 mm. We omitted drying the alcohol over calcium shavings in all our later preparations, as we were unable to procure calcium, which did not contain either carbon or nitrogen. The isobutyl alcohol prepared in this way was undoubtedly much purer than any product that had been previously made. The advantage of purifying the alcohol through the boric ester is not alone that the ester boils much higher than the alcohol, which thus permits the removal by distillation of all substances that have approximately the boiling point of the alcohol but which do not form an ester. It also permits a much sharper separation from the higher and lower

¹ *Ann.*, 393, 104 (1912).

² Counciler, *J. prakt. Chem.*, [2] 18, 382 (1878).

boiling alcohols, that are undoubtedly contained to an appreciable extent in all preparations of isobutyl alcohol purified solely by fractionation, as, according to Counciler's rule,¹ the difference between the boiling points of such alcohols is increased three times in the corresponding boric esters.² Another great advantage in this method of purification lies in the facility with which the boric esters may be saponified. Before using this method we endeavored to purify the alcohol through the benzoate; but, although we obtained a product that boiled absolutely constant, we were unable to saponify it, unless alcohol was used, without the formation of by-products.

In one of our earlier preparations of the bromide we prepared the hydrobromic acid from bromine and phosphorus, the latter substance having been purified by treatment with carbon bisulfide. In one preparation on passing the gaseous hydrobromic acid into the alcohol and acid mixture, a small amount of a white crystalline substance was formed, which showed a decided odor of garlic and was found to contain arsenic. Although no arsenic could be detected in the bromide after its purification, it showed an unusually high value of rearrangement, and there may have been, notwithstanding, traces of an arsenic compound present, which acted as a positive catalyte. In the subsequent preparations of hydrobromic acid using red phosphorus, we employed a product prepared by heating yellow phosphorus, that was freed from arsenic by two distillations with steam, and the bromide always gave smaller reaction values.

In all our later preparations of bromide, we used hydrobromic acid made catalytically from electrolytic hydrogen and bromine that had been carefully purified according to the directions of Baxter, Thorvaldson and Cobb.³ The acid prepared in this way always contained a small quantity of free bromine which was removed by heating the aqueous product, saturated at 0°, after the addition of a sufficient amount of pure iron (such as is used for atomic weight work) and collecting the gas in water; after the gas ceased to come off the residue was distilled and the distillate used as the constant boiling acid.

A mixture of 40 cc. isobutyl alcohol and 40 cc. constant boiling hydrobromic acid was brought into a tube, cooled off to 0°, and saturated with gaseous hydrobromic acid, obtained by warming a saturated acid solution, to which pure iron had been added in sufficient amount to expel

¹ *J. prakt. Chem.*, [2] 18, 385 (1878).

² Cohn, *Pharm. Zentralhalle*, 1911, 482. We modified the method used by this chemist, using only 5% strong sulfuric acid to esterize, but the boric ester prepared in this way could not be obtained in a pure state.

³ *THIS JOURNAL*, 33, 319 (1911). We are greatly indebted to Professor G. P. Baxter for the use of the apparatus and other facilities in his laboratory; also to Mr. F. L. Grover for his kind assistance in the preparation of the acid.

most of the air in the vessel. The operation was done in an apparatus composed entirely of glass, and, to avoid a decomposition of the acid by the ground glass surfaces, in a darkened room. After sealing the tube it was placed in an iron tube closed at both ends, and heated in a water bath for 3-4 hours at 65° . The yield of the colorless bromide was about 60 g.; a small amount was formed on further heating of the tube, but it was found inadvisable to unite it with the main product. The bromide was extracted with about 4 times its volume of water in a shaker, until the last extract ceased to give an immediate reaction with silver nitrate, then dried several days over fused calcium bromide and, finally, an hour or two before the distillation, by addition of a small amount of pure phosphorus pentoxide. The fractionation should be done in a partial vacuum, as the operation under ordinary pressure leads to the formation of some tertiary bromide. For this reason, too, a sharp boiling point of the pure bromide could not be obtained under ordinary pressure; thus, a small quantity boiled between $91.1-91.25^{\circ}$ (755.5 mm.), while absolutely sharp and constant boiling points could be obtained with less pure products only.

All the chemicals used in the preparation of the bromide were as pure as could be made. Phosphoric anhydride was sublimed in oxygen; ordinary distilled water was distilled with addition of permanganate and then redistilled. The glass apparatus was cleaned with a mixture of nitric and sulfuric acids, then thoroughly washed out with water and finally steamed for a long time. The distillation was done in a specially constructed flask with double jacket, in which the thermometer was fastened in the inner tube by a platinum spiral and ground glass stopper. To dry this apparatus the bulb was immersed in a bath of Wood's metal and a glass tube introduced, which reached to the bottom of the bulb and to whose upper end a glass cap was sealed, which fitted on a cork on the neck of the fractionating flask: pure and dry air was then aspirated through the apparatus for a long time. The receivers were always in larger glass vessels, the necks of which were joined to the lateral tube of the fractionating flasks by means of corks.

Altogether eleven preparations of isobutyl bromide were made. In the first seven experiments the method was gradually improved and we found that the reactivity of the products varied accordingly: the last four were practically all made according to the directions given above; slight variations which we tried had no effect on the quality of the products. In the following experiments the preparations used up to VII are designated by Roman numerals; the subsequent products are grouped together under VIII. The first six products could be distilled without change under ordinary pressure in flasks of hard or soft glass, with the exception of a single flask of unknown composition, in which a decomposition, with

formation of hydrobromic acid and also a slight rearrangement to tertiary butyl bromide, was always noticed. The only difference between VII and the later preparations, was that it could be distilled once under ordinary pressure without formation of tertiary bromide or hydrobromic acid. Some of the earlier preparations gradually gave off hydrobromic acid on standing over phosphoric anhydride. Thus, a constant boiling product, after standing several days with the pentoxide, not only evolved some acid, but was colored brown; after extracting with water and drying, it boiled within 0.4° and contained some diisobutene. Our purest products also gave off traces of hydrobromic acid on standing a long time over the pentoxide, which should be, therefore, used with care as a drying reagent.

The most reactive preparation of bromine obtained by Michael and Zeidler¹ was made by heating carefully purified hydrobromic acid and isobutyl alcohol to 75° . This product, after 1 fractionation gave, on heating 1 hour in the vapor of xylene, 15.1% of tertiary bromide and, by repeated fractionation, a product that in some of the experiments gave about 74%, which is near the limit of rearrangement. Preparation VII before distillation yielded 53.1% tertiary bromide in $\frac{1}{2}$ hour in xylene and 63.2% after 1 distillation and in 1 hour also gave 74%. Preparation VIII, undistilled, gave 12.9% of tertiary product after heating $\frac{1}{4}$ hour at 108° and 16.3% after 1 distillation *in vacuo*, which represents the normal rate of rearrangement. We noticed with several of our earlier preparations that the velocity of isomerization could be increased up to a certain point by fractionation and that a subsequent operation led to a decrease. This was very noticeable with III, which, heated $\frac{1}{2}$ hour in xylene, gave before fractionation 11.1% of tertiary bromide and 60.7% after two such operations, while the product obtained in the third process gave only 27.3%, although no decomposition or change could be noticed in the product.

Rearrangement in a Liquid Phase.

The methods used in studying the reaction were about the same as described in the previous papers.² The bromide was usually heated in a short bulb of Jena hard glass, one end of which was round and the other pulled out to a very narrow tube about 10 cm. long. The dried vessels were filled with bromide by means of a pipet, which consisted of a capillary tube, in whose upper end a small bulb was blown. The wide end of the tube was connected with a small U-tube, containing some calcium chloride and whose other side had a glass plunger working through a piece of rubber tubing. The tubes were usually filled to about one-half, so that the bromide was also present in a gaseous phase, but in some experiments the liquid completely occupied the vessel. In the earlier

¹ *Ann.*, 393, 104 (1912).

² *Ibid.*, 379, 304; 393, 94.

experiments the bulbs, before sealing, were connected with small drying tubes containing phosphorus pentoxide; later they were put in narrow, thin test tubes whose open ends were closed by drying tubes, and then placed in a cooling mixture of salt and ice. It was not always possible to prevent the formation of the slight white ring on sealing the containers,¹ but our experiments show that this has no noticeable influence on the result of the rearrangement. In other experiments, we used small Hofmann bottles, made either of soft glass or of quartz, which were enclosed in thin, narrow, sealed glass tubes. The bulbs were heated in the vapor of liquids, which were contained in Meyer vapor density mantels and whose walls were covered with asbestos paper. To determine the amount of tertiary bromide the heated product was put in a shaker for 15 minutes, with 50 cc. water and at first the filtered solution, later the whole liquid, titrated with $N/10$, or $N/25$ solutions, of silver nitrate and ammonium thiocyanate, using ammonium iron alum as the indicator. With 0.1 g. bromide and $N/25$ solutions the determinations were exact to 0.15%.

Normal Rearrangement in Glass and Quartz.

To determine the quality of the bromide, the product was heated for 15 minutes in the vapor of isobutyl alcohol (108°) in Jena hard glass tubes of 6 mm. internal diameter. Four of our best preparations gave the following results:

16.4, 15.7, 16.9, 16.3; mean, 16.3%.

This mean value (16.3%) may be considered as representing the normal rearrangement of isobutyl bromide under these conditions.

The mean value with a bromide of less purity is lower than that of the pure bromide. Thus, some of our earlier preparations gave under the same conditions:

14.0, 15.2, 15.1, 14.3, 15.2, 15.2, 14.0; mean, 14.7%.

After we found that a certain variety of glass shows a decided catalytic influence on the reaction, we made a series of experiments to ascertain whether Jena hard glass also exerts such an effect. For this purpose, we employed small bottles of quartz, with ground stoppers, which were filled to about one-half and enclosed in slightly wider sealed Jena glass tubes with thin walls. The 3 bottles had round bottoms and an internal diameter of 4.3 mm. and an interior height of 4 cm.

The following amounts of tertiary bromide were obtained with VIII:

At 108.4° ,	for 15 min.,	11.7, 10.4, 11.4%;
At 130° ,	for 5 min.,	17.7, 16.8, 15.7%;
At 142° ,	for 10 min.,	41.3, 38.3, 41.8, 41.7%;
At 142° ,	for 20 min.,	56.8% and for 30 minutes 63.3%.

The mean of a number of determinations in hard, as well as in ordinary

¹ *Ann.*, 393, 108.

soft glass tubes of the same diameter as the bottles at 108° for 15 minutes was 12.8%, at 142° for 10 minutes was 45.9%, and for 30 minutes 63%, of tertiary bromide. In the experiments of short duration the mean values are somewhat higher in glass than in quartz, but it is safe to conclude from the results that soft and Jena hard glass exercise no perceptible catalytic influence, as the actual time of heating at the temperature of the bath was evidently somewhat less with the enclosed quartz vessels. In the experiments for 30 minutes the results are practically the same.

We noticed in these experiments that the quartz vessels, even when made of the highest quality of quartz we were able to procure, with continued use gradually showed corroded surfaces. This may have come, however, from the action of the acids used in cleaning the vessels. It is remarkable, too, that the values obtained in the first determination in small Hofmann bottles, whether made of quartz or of glass, were invariably lower than those found in the subsequent experiments; indeed, in quartz vessels we found in several cases that no rearrangement took place at first at 108° .

Influence of Catalytes on the Rearrangement.

Although Jena hard glass and ordinary soft glass, notwithstanding that part of the surface of the latter sort exposed to the liquid, but not to the gaseous bromide, in some experiments was slightly corroded and therefore acted on chemically, has no perceptible influence on the reaction, we found that it is very much accelerated in Jena "Geraete" glass. Thus, in one series of experiments, which were made in tubes of the same diameter, we obtained, at 108° for $\frac{1}{2}$ hour, in Jena hard glass 16.9%, while in "Geraete" glass 44% tertiary bromide was formed. The rate, therefore, was increased almost 3 times. At 100° the highest value we noticed using hard glass (6 mm.) after 30 minutes was 9.2%; in "Geraete" glass, in a narrower tube (4 mm.) after 8 minutes 11.2% and after 15 minutes 39.6% tertiary bromide was formed. The constituent of "Geraete" glass not contained in the other varieties of glass used in these experiments is ZnO and to the amount of 4.2%.¹ It seemed probable, therefore, that the catalytic action of this glass is due to the zinc it contains. To test this inference we made some experiments with the addition of ZnBr_2 . For this purpose, we introduced 1 drop of a dilute solution of ZnBr_2 into bulbs of hard glass, heated the tubes carefully while aspirating dry air through them until they were perfectly dry and then performed the experiments in the usual manner. Without ZnBr_2 , 14.7%, with it, 23.6 and 25.9% tertiary bromide was formed. According to a determination a drop of the ZnBr_2 solution contained 0.00002 g. of salt; and as 0.2 g. bromide was used, the addition of about 0.0001% of this catalyte, therefore, almost doubled the velocity of the reaction. A similar experiment, made

¹ *Ost. Lehrb. d. Chem. Technol.* (6 Auflage), 279.

under the same conditions but using four drops of the salt solution, gave 32.6% tertiary bromide, while with the ZnBr_2 contained in 12 drops it caused the formation of dark by-products. Indeed, the addition of ZnBr_2 in appreciable amount prevents the rearrangement completely, which is probably due, however, to the secondary products formed under such conditions. We thought it possible that the reagents used in cleaning the tubes of "Geraete" glass might show an influence on the rate of rearrangement, but failed to notice a difference in the results of the experiments, whether a mixture of bichromate and sulfuric acid, or concentrated hydrobromic acid, was used. Although it may be considered certain that the catalytic action of "Geraete" glass is due to the presence of zinc we were unable to ascertain whether it is owing to the action of the glass *per se*, or to the formation of a simpler zinc compound by the chemical action of isobutyl bromide in the glass. It is certain, however, that the zinc in this glass is very resistant to the action of strong chemicals, for some of the powdered material was heated for some time with concentrated hydrobromic acid and no zinc could be detected in the liquid. If a soluble zinc compound is formed during the heating of isobutyl bromide in a closed vessel of "Geraete" glass the amount is certainly infinitesimal in quantity, since we boiled the bromide in a "Geraete" glass vessel for a considerable time and could not notice a solid residue on evaporation of the liquid in a platinum dish.

That the catalytic effect of "Geraete" glass varies very considerably, will be seen from the following experiments, where, although the vessels were all made from the same piece of tubing, no relation appears between the time of heating and the extent of rearrangement, unless the latter values were quite small.

At 80.5° , in tubes of 4 mm. internal diameter:

20	40	60	80	minutes
8	11.7	15.2	8.9%	tertiary bromide

At 108° , in tubes of 8 mm. diameter:

5	10	15	25	minutes
24.0	39.7	22.3	37.5%	tertiary bromide

We also noticed that the use of the same container of "Geraete" glass a second time was followed by a decrease of its efficiency as a catalyte, which remained then unimpaired in subsequent experiments.

In acetone (56°); new tubes:

1	2	3	hours
4.4	4.5	5.3%	tertiary bromide

In methyl alcohol (66°); tubes used a second time:

10	20	30	90	135	minutes
0.6	1.0	1.4	3.7	4.0%	tertiary bromide

Although the temperature in the second series was 10° higher the rearrangement values are less.

In methyl alcohol (66°); tubes used a third time:

30	60	90	minutes
1.5	2.8	3.7	%

Another salt, which acts as a positive catalyte on the rearrangement of isobutyl bromide, is mercuric chloride. This salt dissolves in the bromide to the extent of about 1.5%; such a solution after standing four days in summer at room temperature did not give the test for tertiary bromide, but the reaction proceeds readily at a somewhat higher temperature. As with the use of zinc bromide, we were not only unable to find a direct connection between the time of heating and the extent of the rearrangement, but the results were sometimes quite irregular among themselves. Thus, a series, where the bromide contained 0.07% sublimate, resulted as follows:

10	20	40	60	90	minutes at 78.3°
9.5	31.5	24.1	35.4	34.8	% tertiary bromide
	22.7				

Mercuric chloride, like zinc bromide, acts catalytically only in very dilute solution; in the vapor of alcohol 0.3% sufficed to prevent the reaction. A series, heated 40 minutes at 78.3° , gave

0.02	0.15	0.3	% mercuric chloride
12.7	41.2	0.0	% tertiary bromide

Calcium bromide exerted no influence on the rearrangement; nor did aluminium oxide, probably because the bromide does not react on it, as the formation of aluminium bromide, even in traces, would have been undoubtedly followed by a marked reaction.¹

Hydrochloric acid, however, shows a decided catalytic influence, even at ordinary temperature. Isobutyl bromide, which was saturated with the dry acid (about 0.3%) contained 3% tertiary bromide after standing two days. In the following series a quantity of such a solution was heated to 56° , in a carefully ground, glass-stoppered vessel and from time to time a sample was removed for analysis:

$1\frac{1}{2}$	1	$1\frac{1}{2}$	2	$2\frac{1}{2}$	$3\frac{1}{2}$	11	hours
9.5	12.3	14.9	17.0	18.3	19.7	25.1	% tertiary bromide

These results are more regular than those in the preceding experiments and further investigation is necessary to determine whether this is due to their being carried out in the same vessel, or to the nature of the catalyte.

In their experiments on the influence of negative catalytes on the rearrangement, Michael and Zeidler² used tubes filled to about one half with the solution and the substance was, therefore, in a gaseous-liquid

¹ Kekulé and Schroetter, *Ber.*, 12, 2279 (1879); Gustavson, *Ibid.*, 16, 958 (1883).

² *Ann.*, 393, 105 (1912).

state. In connection with the results described below on the reaction entirely in the liquid phase, we made some experiments, using negative catalytes under the same conditions. We found that the addition of diisobutene reduced the rate of the reaction very considerably. Thus, in hard glass tubes, which were entirely filled with isobutyl bromide (VIII), the rearrangement after 1 hour at 108° was 14.0% for the liquid in the narrow tube and 12.6% for the part in the bulb; with bromide containing 2.6% diisobutene the result was 6.2 and 5.2% for the narrow tube and 3.7 and 4.0% for the bulbs. A solution containing 1.3% of the hydrocarbon gave approximately the same results, *i. e.*, 7.4 and 5.5% in the contracted and 4.4 and 4.3% in the wide part of the containers. Further experiments were made with one of the earlier preparations of bromide; heated for 1 hour at 108° the mean value of a number of experiments was 13.7% for the liquid in the bulb. The addition of the following chemicals showed a marked reduction:

2.6% diisobutene	3.6 : 3.7% tertiary bromide
3.7% tertiary butyl alcohol	3.5 : 3.5% tertiary bromide
3.2% isobutyl alcohol	3.2 : 3.1% tertiary bromide

These low values are also probably near the limit of the reaction under these conditions, as heating tubes containing the same percentage of diisobutene for 2 and 4 hours gave only 4.0 and 4.1% of tertiary product.

Under the same conditions, a trace of water added to the bromide exerted scarcely any influence on the rearrangement.

Influence of Air on the Rearrangement.

In the preceding experiments the tubes were only partially filled with liquid bromide, so that the reaction occurred in the presence of a gaseous phase and also of air. The determination of the rearrangement of the bromide solely in a liquid phase should give, therefore, information whether air exerts an influence and, also, on the mechanism of the reaction.

In our first experiments the bromide was brought into bulbs of Jena hard glass (6 mm.) with narrow ends about 20 cm. long. These were filled until the liquid occupied about $\frac{1}{2}$ of the narrow tubes and after sealing the bulbs alone were heated in the bath. The contents of the bulbs gave the following values:

30 minutes at 108° , 11.5, 10.0, 8.5	% tertiary bromide
60 minutes at 108° , 11.3, 11.9, 11.8, 12.1	% tertiary bromide
120 minutes at 108° , 16.9, 13.6, 15.4	% tertiary bromide

The transpiration of the tertiary bromide during the heating was inconsiderable, as not more than 1% tertiary bromide was found in the liquid contained in the narrow ends.

As we noticed that isobutyl bromide heated under pressure has the property of absorbing a small amount of air, we made use of this property to examine the influence of air on the reaction and, at the same time,

the rearrangement in the liquid phase. The bulbs were like those used in the above experiments, only the narrow ends were somewhat shorter (about 15 cm.); they were filled with bromide to 15–20 mm. from the open end and the expansion of the liquid on heating made it occupy the entire container. In several experiments a small amount of air remained unabsorbed, but no difference in the results was noticed. After heating the entire vessels to 108° the contents of the bulbs B and of the narrow ends C were analyzed separately.

30 minutes.		60 minutes.		
B.	C.	B.	C.	
11.8	14.6	12.5	14.2	% tertiary bromide
13.8	15.7	12.8	14.0	% tertiary bromide
11.3	13.1	12.4	14.0	% tertiary bromide
11.4	11.7	12.5	13.6	% tertiary bromide

Heating for 2 and 4 hours gave 15.4 and 18.6% for B and 18.7 and 20.1% for C. These experiments show that the greater proportion of air in the bromide contained in the narrow ends causes a slight increase in the rate of rearrangement, and any relative increase of the surface of the bromide exposed to air to the amount of liquid used should, therefore, increase the velocity of the reaction, if the bromide is not saturated. This relation is plainly noticeable in the results of the following series, in which the container was modified to increase the surface of liquid exposed to air. About 10 cm. above the bulb a second bulb was blown in the narrow end and bromide introduced until the upper bulb was half full. After sealing the entire vessel was heated and the contents of the lower and that of the upper bulb, with the small amount in the capillary tube joining the two bulbs, analyzed separately. The temperature was 108° and time of heating 1 hour.

Diameter of bulbs.....	7.5	7.0	6.5	mm.
Capillary tube and upper bulb.....	19.0	17.7	16.9	% tertiary bromide
Lower bulb.....	12.3	13.1	13.5	% tertiary bromide

The mean values for the upper and lower bulbs in these experiments are 17.9 and 13.3%, while in the preceding series, where less surface was exposed to the air, they were 14.0% for the narrow tubes and 12.6% for the bulbs.

That with more surface of bromide exposed to air the velocity of the isomerization increases was proven by Michael and Leupold,¹ but we deemed it of interest to repeat the experiment with our purer bromide. A bulb (6 mm. diam.) and a narrow tube (about 1 mm.) were filled to one-half with bromide and heated together; the contents of the bulb contained 55.9% and that of the tube 19.3% tertiary product. Tubes of 6 and 1.2 mm., internal diameter, heated for $\frac{1}{2}$ hour at 140° , gave the following results:

¹ *Ann.*, 379, 306.

1.2 mm.	6 mm.	
37.4	63.2	% tertiary bromide
43.7	55.9	% tertiary bromide

We next endeavored to modify the conditions so that isobutyl bromide free of air could be heated either entirely in a liquid phase, or in presence of a vacuum. For this purpose, some bromide was brought into a small retort-shaped glass vessel, which was held in a slanting position, and empty bulbs, with the narrow open ends facing downwards, introduced so that they remained in the limb of the vessel. The open end fitted closely for several inches into a glass tube, ending in a glass stopcock, which was bent at a right angle and was connected to it by a piece of rubber tubing. The liquid was cooled off in ice and the apparatus connected with a Geryk vacuum pump and evacuated until about $\frac{1}{2}$ of the bromide had evaporated, when the stopcock was closed and disconnected from the pump. The apparatus was then placed upright and the open ends of the bulbs brought under the liquid. On allowing dry air to enter slowly into the apparatus, the bulbs became completely filled with bromide. The open ends of the bulbs were then connected with a vacuum pump and either sufficient bromide evaporated in a vacuum so the expansion to the liquid completely filled the tube when it was sealed and heated, or so much more that a vacuum remained in the narrow ends above the liquid. The experimental difficulties in these experiments were considerable and the results are not as concordant among themselves as those obtained in some of the previous series. At 108° for 15 minutes, the mean percentage of a number of experiments was in the liquid phase alone 11.6% and in presence of a vacuum it was 11.4%. It may be concluded, with considerable probability from these results, that there is little or no difference in the rearrangement of isobutyl bromide, when it is in a liquid, or in a liquid-gaseous condition, and they confirm, therefore, the conclusion from simpler and more decisive experiments. Furthermore, a comparison of these values, with the normal value in the presence of air, which is 12.8% under the same conditions, corroborates the previous conclusion that air acts as a positive catalyte on the rearrangement.

Influence of Ground Surfaces on the Rearrangement.

Abnormal results are obtained when the bromide is heated in small Hofmann bottles with ground glass stoppers, whether they are made of soft glass or of quartz. In the following experiments, the interior dimensions of the bottles employed were 17 mm. high and 4 mm. wide and they were heated 1 hour at 108° .¹

Rearrangement.	In entirely liquid phase.	With air.
Glass.....	5.3, *5.9, *4.3, 5.4%	13.4, 11.3, 10.5*%
Quartz.....	1.8, 1.7, 2.2, 2.1%	4.5, 3.9,* 2.9*%

¹ The figures without asterisks were obtained, using the same bottle; those which have a single mark were made in different ones.

These results show that not only is there a considerable difference between the values obtained in glass and in quartz, but, also, when the bromide is present solely in a liquid state and when air is present, although there were only small bubbles in the vessels. The influence of ground surface in decreasing the rearrangement is shown very markedly in the following series of experiments, where, in the presence of air, the bromide was heated in a quartz bottle with a long narrow neck (6 cm.), whose bulb was only partially filled with liquid, and in a completely filled Hofmann bottle of quartz.

Short bottle: 4.2, 4.2, 5.0% after $\frac{1}{2}$ hour

Long bottle: 11.7, 10.4, 11.4% after $\frac{1}{4}$ hour

We noticed that bromide kept in bottles with ground glass stoppers gradually became somewhat colored and that the coloration was quite marked at the ground surfaces, which had, evidently, slowly decomposed the substance. Traces of such decomposition products are probably formed on heating the bromide, when it is in contact with ground surfaces, and they act as negative catalytes. In the presence of air in a small Hofmann bottle the liquid comes much less in contact with the ground surface, and still less in the long neck vessels, and there is, therefore, a corresponding decrease in the formation of by-products. Even at a higher temperature and with air space the percentage of rearrangement in a Hofmann bottle of quartz is slow; thus for 1 hour at 184° only 3.3, 4.2 and 6.9% tertiary bromide were formed, while 67% was obtained in a glass bulb, under the same conditions.

Rearrangement in Gaseous Condition.

A thin, sealed bulb containing isobutyl bromide was brought into a wide glass tube, which was then evacuated to 1 mm. pressure and sealed, when the bulb was broken. The tube was heated, then cooled off in a freezing mixture, the contents washed out with water and alcohol and the analysis made in the usual manner. The results are 2-3% low, as there is a mechanical loss in the manipulation.¹

Heating 3 hours at 100° gave 2.3% tertiary product; 25 minutes at 184° , in a tube of Jena hard glass, gave 34.0% and in one of a soft glass 53.5%. These results are very much higher than those Michael and Leupold² obtained with their product, who noticed no change on heating to 142° for 14 hours and only 2.7% at 184° for $2\frac{1}{2}$ hours, and they show how markedly the reaction in gaseous condition depends on the purity of the isobutyl bromide.

Vapor Density Determinations.

V. Meyer's method was used, but care was taken to carry out the operation in a dry atmosphere, as Konowalow³ believed that moisture affects

¹ Michael and Leupold, *Ann.*, 379, 313.

² *Ibid.*, 379, 314 (1910).

³ *Ber.*, 18, 2808 (1885).

the results. The apparatus was thoroughly cleaned after each determination, carefully dried and the evolved gas collected over 70% sulfuric acid.

In the following two determinations Hofmann bottles of quartz were used, which were introduced into the apparatus through a Mahlmann stopcock; the bottom of the Meyer tube was covered with very thin rods of Jena hard glass. The temperature of the bath was 142°.

	I.	II.
Substance.....	0.0944 g.	0.1185 g.
Volume of gas.....	18.03 cc.	22.23 cc.
Pressure.....	757.0 mm.	760.5 mm.
Temperature.....	26.4°	25.5°
Found density.....	68.7	69.1
Calculated density.....	68.5	68.5

The volume of evolved gas became constant after several minutes and then underwent no change, even though heated for $\frac{1}{4}$ hour. After cooling, the Meyer tube was washed out with alcohol and the amount of tertiary bromide present determined in the usual manner; in I 2.4% and in II 5.0% was found, which results are probably several per cent. too low.

In other similar experiments after the volume of gas remained constant, we introduced sand and asbestos, which, according to Konowalow¹ act catalytically on the dissociation of tertiary amyl chloride and other analogous compounds. The addition of these substances had no effect; nor did powdered "Geraete" glass, which accelerates the rearrangement of liquid isobutyl bromide so greatly.

The following determinations were done at 184°; in I a quartz, in II a Jena hard glass, Hofmann bottle was employed, and in both experiments the bottom of the Meyer tube was uncovered; in III a hard glass bottle was used, and there were thin rods of the same material in the apparatus.

	I.	II.
Substance.....	0.1223 g.	0.0942 g.
Pressure.....	763.5 mm.	762.8 mm.
Temperature.....	21.3°	22.6°
Volume of gas.....	23.1, 33.5 cc.	18.05, 25.85 cc.
Height of acid.....	30.1, 20.6 cm.	34.8, 27.6 cm.
Found densities.....	66.8, 45.4	66.7, 45.9
Dissociation.....	Above 50%	

I and II were done with the same preparation (VIII); Experiment III, which was done with a different one, gave a final density of 48.5. After heating about one minute in all the determinations, the rapid evolution of gas ceased, and the volumes corresponded to about that of the normal density; then a slow generation of bubbles kept up for about 15 minutes.

CAMBRIDGE, MASS.

¹ Ber., 18, 2808.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

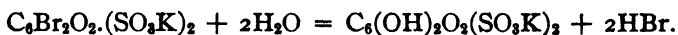
CERTAIN DERIVATIVES OF TETRABROMO-*o*-QUINONE.¹

By C. LORING JACKSON AND SYDNEY A. BEGGS.

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This paper contains an account of our study of the behavior of tetrabromo-*o*-quinone with dipotassium sulfide, and with dimethylamine.

When a solution of tetrabromo-*o*-quinone in benzene is shaken with aqueous dipotassium sulfide, the principal product is potassium dibromopyrocatechindisulfonate, $C_6Br_2(OH)_2(SO_3K)_2$, from which we prepared the barium salt $C_6Br_2(OH)_2(SO_3)_2Ba \cdot 3H_2O$, and the calcium salt $C_6Br_2(OH)_2(SO_3)_2Ca \cdot 4H_2O$. If this potassium salt was moistened with strong nitric acid with careful cooling, a red product was obtained, which we think is potassium dibromo-*o*-quinonedisulfonate, $C_6Br_2O_2(SO_3K)_2$, contaminated with a little potassium nitrate, which we were unable to remove. This substance dissolved in cold water, a little less than a gram being taken up by 1 cc. of water; but, if the solution stood overnight at ordinary temperatures, it deposited much less soluble red crystals of the tripotassium euthiochronate, which was identified by conversion into the tetrapotassium salt, when the characteristic change of color with analyses of this latter salt left no doubt about the nature of the substance.



After this reaction had taken place the dioxyorthoquinone would at once change to the more stable *p*-quinone (euthiochronic acid) according to all the observations of similar cases. The euthiochronate was also formed by the action of potassium hydroxide solution.

Our reasons for believing that the immediate product from the action of nitric acid contains an orthoquinone group are: its red color, the ease with which water converts it into a euthiochronate, and the extreme activity of the atoms of bromine in it, since they are removed from it by water at ordinary temperatures, whereas the original potassium dibromopyrocatechindisulfonate gave up no bromine even to boiling water, and with a solution of potassium hydroxide it was necessary to heat in order to form the euthiochronate. That the orthoquinone group has a very vigorous action in loosening halogen atoms associated with it has been shown by all our experience. The objection that the red color of our product may be caused by the presence of tripotassium euthiochronate is met by the observation that the solution of our salt deposits crystals of the euthiochronate on standing for some hours, so that it must be less soluble than our product, and seems to be formed from it gradually by the action of water.

¹ The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by Sydney Adams Beggs.

As it seemed probable that so negative an *o*-quinone as the potassium dibromo-*o*-quinonedisulfonate would behave like tetrabromo-*o*-quinone, we tried some experiments in the hope of obtaining α -addition compounds¹ from it; but after six months no action could be observed with ethyl, or benzyl alcohol, and although methyl alcohol gave a white product, its amount was too small to determine its nature.

The potassium dibromo-*o*-quinonedisulfonate, when made with nitric acid, contained an impurity of niter, as already mentioned. In the hope of obtaining it free from impurity we exposed potassium dibromopyrocatechindisulfonate to electrolytic oxidation, but although the quinone salt was formed, as shown by the red color, we could not obtain it in this way, since by the time the pyrocatechin salt was completely oxidized the greater part of the red quinone salt had been destroyed, showing that it is as susceptible to oxidation as its mother substance. If the action was continued, till the red color had gone, most of the organic matter seemed to have been burnt up, but a small yield of pentabromoacetone was obtained. This was recognized by bromine and molecular weight determinations, which were necessary, as we found its melting point 73–74° (uncorr.), whereas it is given by Beilstein as 76°. In a research on hexabromodiacetyl² Adams and one of us also encountered pentabromoacetone, and entirely independently found its melting point 73° (uncorr.). An examination of the work of others on this subject shows that we are not alone in this experience, Wilde³ giving 71–72°, Wichelhaus⁴ 74°, Steiner⁵ 74°, while the higher melting points were obtained by Benedikt⁶ 76°, and Zincke and Kegel⁷ 76–77°. The explanation of these discrepancies is probably to be found in the observation of Benedikt that the alcoholic solution of pentabromoacetone, although neutral at first, in a few hours becomes acid and smells of bromoform. In all the cases with lower melting points the crystallization was carried on in alcohol, and enough impurity may have been formed to lower the melting point, although it did not show in the analyses in any case except Steiner's, whose product was so impure that the analyses misled him at first in regard to its nature.⁸ The highest result—that of Zincke and Kegel—was obtained after crystallization from ether and benzene. Benedikt speaks of crystallizing from alcohol or chloroform. If our explanation is correct his melting point was probably taken after the use of the latter.

¹ Jackson and Porter, *Am. Chem. J.*, 31, 89 (1904).

² *THIS JOURNAL*, 37, 2532 (1915).

³ *Ann.*, 127, 167 (1863).

⁴ *Ibid.*, 152, 260 (1869).

⁵ *Ber.*, 7, 505 (1874).

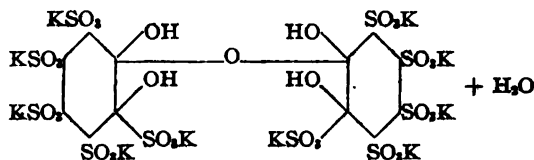
⁶ *Ann.*, 189, 168 (1878).

⁷ *Ber.*, 23, 1725 (1890).

⁸ Steiner, *Ibid.*, 7, 1284 (1874).

As already stated, when a solution of dipotassium sulfite was shaken with a benzene solution of tetrabromo-*o*-quinone, the product was potassium dibromopyrocatechindisulfonate, but with this there was formed a small quantity of another white salt, which could be made the principal product of the reaction by heating the solution of the dipotassium sulfite to 50° before shaking it with the benzene solution of tetrabromo-*o*-quinone instead of carrying on the reaction in the cold. In this connection we had the strange experience of finding we could not prepare this new salt for nearly a year, the potassium dibromopyrocatechindisulfonate being the only product obtained under conditions which both before and after it gave the new compound invariably. In spite of a careful study we are able to give no explanation of this phenomenon.

The complete analysis of this compound led to the formula $C_6(SO_2K)_6O_2H_2$, or some multiple of it, which would make it the *o*-thiochronate retaining like the corresponding para compound one molecule of water at 130° (4 molecules of water were lost below 130° leaving the formula given above). We cannot, however, accept this view of its constitution for the following reasons: The *p*-thiochronate has a distinct yellow color, and in view of the fact that *o*-quinones are more highly colored than *p*-quinones, the *o*-thiochronate should be red, but the new compound is white. The thiochronate is easily converted into a euthiochronate by potassium hydroxide; the new compound can be boiled with a strong solution of this reagent without change. Hydrochloric acid also reacts with the thiochronate, when boiled with it, but the new compound is unaffected by it below 150°, at which temperature it is completely charred. The thiochronate gives an intense brown-red color with ferric chloride; the new compound barely deepens the yellow color of the reagent and it does not reduce a solution of a silver salt, whereas the thiochronate does. The α -water addition compound¹ of the *o*-thiochronate containing one molecule of water of crystallization should have all the



properties enumerated above except the indifference to boiling hydrochloric acid, since the water compound of tetrabromo-*o*-quinone is affected by this reagent, but as the action consists in the formation of chlorine, and therefore is evidently due to the free carbonyl in the bromine compound, which does not exist in our salt, the difference does not tell strongly against our formula. Further, such a derivative would be expected from

¹ Jackson and Porter, *Am. Chem. J.*, 31, 109 (1904); Jackson and MacLaurin, *Ibid.*, 37, 87 (1907).

the *o*-thiochronate, if this were the first product of the reaction, as the molecule is highly charged with negative radicals, which, so far as is known, favor the formation of these addition compounds. As already stated it is necessary to assume the presence of a molecule of water even at 130°, but this does not tell against our formula, as Graebe¹ found that the thiochronate also retains a molecule of water at such high temperatures. We have adopted provisionally this formula for the substance for the reasons given above, but it must be remembered that it cannot be finally accepted, until it has been confirmed by additional experiments.

As aniline gave a number of well-marked derivatives² with tetrabromo-*o*-quinone, we thought that equally good results might be obtained by the action of secondary amines, but our experiments in this direction were disappointing. Methylaniline gave only a tar, although we tried a great many conditions of temperature solvents and proportions; and from dimethylamine we obtained only one product in unstable black crystals, thrown down when it was passed into a solution of tetrabromo-*o*-quinone. Its formula is probably $C_6Br_4O_2(NH(CH_3)_2)_2$. The tetrachloro-*o*-quinone gave a corresponding product. They seem to belong with the similar addition compounds sometimes classed with the quinhydrones.

Experimental.

Action of Dipotassium Sulfite on Tetrabromo-*o*-quinone in the Cold. Dibromopyrocatechindisulfonic Acid.—The dipotassium sulfite used in this work was prepared by dissolving 112 g. of potassium hydroxide in 100 cc. of water, and passing into the solution the sulfur dioxide obtained from 120 g. of acid sodium sulfite with dilute sulfuric acid. Care must be taken that none of the sodium salt spatters over into the potassium salt solution. Upon diluting to 316 cc. a solution was obtained, 2 cc. of which contained 1 g. of K_2SO_3 .

Fifty-six cc. of this solution diluted to 100 cc. were placed in a 250 cc. Erlenmeyer flask, and, after cooling with ice to about 10°, 10 g. of tetrabromo-*o*-quinone dissolved in 60 cc. of benzene were added, the two liquids thoroughly shaken together, and immediately filtered to remove a small amount of white scum that formed at the surface of contact. In the filtrate it was observed that the red color had been transferred from the benzene to the aqueous liquid showing that a reaction had taken place, but on standing for 15 to 30 minutes this red color gradually disappeared from the sulfite solution also, and crystals were deposited, the amount of which increased on standing overnight. These white needles were purified by crystallization from water. Some drying experiments showed that the salt was free from water of crystallization. It was dried at 120° for analysis.

¹ *Ann.*, 146, 40 (1868).

² Jackson and Porter, *Am. Chem. J.*, 30, 518 (1903).

Subs., 0.1422, 0.1777, 0.1794; AgBr, 0.1036; K_2SO_4 , 0.0611; $BaSO_4$, 0.1629 by the method of Carius.

Calc. for $C_6Br_2(OH)_2(SO_3K)_2$: Br, 31.75, K, 15.52, S, 12.70. Found: Br, 31.00, K 15.44, S 12.47.

The substance is therefore potassium dibromopyrocatechindisulfonate.

Properties.—It crystallizes in clusters of white needles, easily soluble in hot water, less so in cold; insoluble in alcohol, or ether. Lead acetate throws down from its solution a white lead salt, which is slightly soluble in water, but as this undoubtedly contained basic salt, it was not analyzed. Silver nitrate is reduced by it on standing. Ferric chloride gives a deep blue color with it. A hot solution of potassium hydroxide turns it dark brown, and converts it after boiling for two hours into potassium euthiochromate, recognized by its characteristic color reactions.

Barium Dibromopyrocatechindisulfonate, $C_6Br_2(OH)_2(SO_3)_2Ba \cdot 3H_2O$.—It was a matter of some difficulty to obtain this salt free from potassium. The lead salt precipitated with lead acetate from a hot concentrated solution of the potassium salt was so gelatinous that a considerable amount of potassium acetate was retained by it, and this was only partially removed by boiling the precipitate 3 or 4 times with small quantities of water, and these boilings could not be continued beyond this on account of the solubility of the lead salt in hot water, which, however, was not great enough to permit its purification by crystallization.

At last we proceeded as follows: The lead salt made and partially freed from potassium acetate as described in the last paragraph was mixed with a little cold water, and treated with a slight excess of dilute sulfuric acid. After the mixture had stood for some time with occasional stirring, the lead sulfate was filtered off, and the filtrate shaken with barium carbonate. It was then warmed on the steam bath to complete the reaction and drive off the carbon dioxide, and the filtrate was evaporated to dryness, after which it was crystallized once from hot water, when it was found by the flame test that the impurity of potassium salt had been removed.

Subs., air dried, 0.3094, 0.2288, 0.3090. Loss at 110° , 0.0277, 0.0198, 0.0268. Subs. dried at 110° , 0.2835, 0.2815; $BaSO_4$, 0.1174, 0.1142.

Calc. for $C_6Br_2(OH)_2(SO_3)_2Ba \cdot 3H_2O$: H_2O , 8.75. Found: H_2O , 8.95, 8.66, 8.67.

Calc. for $C_6Br_2(OH)_2(SO_3)_2Ba$: Ba, 24.39. Found: Ba, 24.32, 23.85.

It is a white, crystalline salt, more soluble in hot water than in cold; insoluble in alcohol.

Calcium Dibromopyrocatechindisulfonate, $C_6Br_2(OH)_2(SO_3)_2Ca \cdot 4H_2O$.—This substance was made in the same way as the barium salt except that the purified lead salt was treated with an amount of dilute sulfuric acid insufficient to act on all the lead. The filtrate, after a small portion had shown the absence of sulfuric acid by the usual test, was treated with calcium carbonate, and purified in the same way as the barium salt.

Subs., air dried, 0.4467, 0.3005. Loss at 120°, 0.0569, 0.0384.

Calc. for $C_6Br_2(OH)_2(SO_3)_2Ca \cdot 4H_2O$: H_2O , 13.39. Found: H_2O , 12.74, 12.78.

Subs. dried at 120°, 0.2352; $CaSO_4$, 0.0676.

Calc. for $C_6Br_2(OH)_2(SO_3)_2Ca$: Ca, 8.59. Found: Ca, 8.45.

It is a white crystalline solid, easily soluble in water; insoluble in alcohol.

Our attempts to prepare dibromopyrocatechindisulfonic acid failed because of the instability of the acid. The solution obtained from the lead salt with insufficient sulfuric acid turned red, even when evaporated at ordinary temperatures whether spontaneously, or by means of a blast of air, and although the residue was white, it evidently was not a sulfonic acid, and could be obtained only in very small quantity. Sulfuretted hydrogen even on long standing gave only a slight decomposition of the lead salt, and we did not succeed in freeing the filtrate from colloidal lead sulfide.

Action of Nitric Acid on Potassium Dibromopyrocatechindisulfonate.—

Five grams of the finely pulverized salt were thoroughly cooled in a glass dish immersed in ice, and moistened with strong nitric acid, when the appearance of a red color showed that a reaction had taken place. To complete this the mixture was allowed to stand for some time in the ice, as at ordinary temperatures the first product is decomposed. When the mass became stiff and pasty, it was ground with a pestle to bring the acid into contact with the salt as completely as possible; and when in spite of the cooling red nitrous fumes began to come off rapidly, the action was stopped by the addition of alcohol, and afterward the mass was washed thoroughly with alcohol. We could find no method of freeing this substance from an impurity of potassium nitrate, as the only solvent for it was water, and this decomposed it even in the cold.

On one occasion a specimen was obtained, which gave a percentage of potassium only about 1% higher than that required by potassium dibromo-*o*-quinonedisulfonate, $C_6Br_2O_2(SO_3K)_2$, and this specimen contained an impurity of niter, as was shown by the diphenylamine test. About 4 g. of the crude red salt were obtained from 5 g. of the pyrocatechin salt. Our reasons for considering this product a quinone are given in the introduction.

The greater part of 5 g. of the red salt dissolved in 5 cc. of cold water, but if the filtered solution was allowed to stand overnight, it deposited red crystals, which were obviously different from the quinone salt, as they were so much less soluble. In one experiment these crystals weighed 0.8 g., and 0.7 g. in addition was obtained by evaporating the filtrate to half the original volume; but further evaporation gave only a tarry residue. This new red salt was free from bromine, and was recognized as tripotassium euthiochronate by the addition of potassium hydroxide, which converted it into the yellow tetrapotassium salt, and this gave the following results on analysis:

Calc. for $C_6O_2(OK)_2(SO_3K)_2 \cdot H_2O$: H_2O , 3.86. Found: H_2O , 4.25, 4.46.

Calc. for $C_6O_2(OK)_2(SO_3K)_2$: K, 34.57. Found: K, 34.60.

Our analyses of the tripotassium salt gave unsatisfactory results, apparently from the formation of some tetrapotassium salt during its attempted purification by crystallization from water.

Specimens of the crude potassium dibromo-*o*-quinonedisulfonate were allowed to stand with methyl, ethyl, and benzyl alcohols in the hope of obtaining α - or β -addition compounds similar to those obtained from tetrabromo-*o*-quinone,¹ and after 6 months it was found that a white crust had formed on the surface of the specimen with methyl alcohol, but no action was visible in the other two experiments. This may have been the desired α -addition compound, but the amount was too small for us to determine its nature. Owing to the insolubility of the salt in alcohol such a sluggish action would be expected here, but we could devise no way of hastening it, since the salt is decomposed by water, in which alone it is soluble.

Electrolytic Oxidation of Potassium Dibromopyrocatechindisulfonate.—This work was undertaken in the hope of preparing the orthoquinone salt in a state of purity. Five grams of the dibromopyrocatechindisulfonate were dissolved in 125 cc. of water, and put in a porous cup surrounded by the same solution. The anode, a square piece of platinum foil, was immersed in the cup, and a current of about 0.8 ampere was passed through the solution, which turned red, indicating the formation of the *o*-quinone salt, but we did not succeed in isolating it, because tests showed the presence of the pyrocatechin salt also, and owing to the easy decomposition of the quinone salt it could be obtained pure only as the direct product of the reaction, any attempt to crystallize it from water converting it into the euthiochronate. As the pyrocatechin salt disappeared from the solution, the red color also vanished, and after passing the current for 24 hours the only product we could find was a white solid insoluble in water. Most of the salt seemed to have been burnt up, however, as the average yield of the white product was 0.15–0.3 g. from 5 g. of the salt. This substance, which contained no sulfur, was crystallized from dilute alcohol, until it showed the constant melting point 73–74° (uncorr.), when it was proved to be pentabromoacetone by the following determinations:

Calc. for $CBBr_5COCBr_5H$: Br, 88.31; M. W., 453. Found: Br, 88.51, 88.76; M. W., 444, 412.

The reason for our low melting point (73–74° instead of 76°) has been considered in the introduction.

Action of a Warm Solution of Dipotassium Sulfite on Tetrabromo-*o*-quinone.—When tetrabromo-*o*-quinone was treated with a cold solution

¹ Jackson and Porter, *Am. Chem. J.*, 31, 89 (1904).

of dipotassium sulfite, the principal product was potassium dibromopyrocatechindisulfonate as already described, but in addition to this there was also formed a minute amount of another substance crystallizing in white plates, which differed from the principal product in that it gave an insoluble barium salt, and remained colorless with ferric chloride (instead of turning blue), and with nitric acid (instead of giving a red color). By carrying on the reaction at a higher temperature this new compound became its principal product. 28 g. of dipotassium sulfite dissolved in 100 cc. of water were heated to 50°, and shaken with 10 g. of tetrabromo-*o*-quinone dissolved in 60 cc. of benzene. The red color was transferred from the benzene to the aqueous solution, but on standing overnight it disappeared entirely, and white crystals were deposited. The strength of the sulfite solution does not affect the product, the same compound being obtained with 200 cc. or 56 cc. of water. 50 g. of tetrabromo-*o*-quinone yielded about 35 g. of the crude product.

Our experience with this preparation was very strange. We tried it first in the spring of 1912, and in the autumn of the same year we studied the effect of different conditions of temperature and concentration on the process, and found that by varying the temperature we could prepare at will either the new substance, or potassium dibromopyrocatechindisulfonate. We accordingly used our supply of the new compound freely, but when in December we tried to make more of it, we could get nothing but potassium dibromopyrocatechindisulfonate under conditions which had given the white substance in quantity in our earlier work. We next made a careful study of all the conditions of the reaction, but no changes in the temperature, concentration of the solutions, or nature of the preparations of the tetrabromopyrocatechin or dipotassium sulfite led to the desired result. In every case the product was the potassium dibromopyrocatechindisulfonate. In the autumn of 1913, however, we repeated the preparation, and then obtained the new compound again without difficulty by the method described above. The only differences we could find between the experiments that gave the substance and those which did not were that they were carried on in the autumn instead of in December and the following months, and in a different room in the same building in the later cases. More work is necessary to explain this interesting experience, but we think the explanation will not be found in any slight variations of the conditions of the process, as our careful study of these led to no result.

The process began to yield the new substance again, after our work together had come so nearly to an end that our investigation of it is of necessity somewhat meager. It was purified by 3 crystallizations from hot water, when it was found to combine no bromine.

Subs., 0.3664, 0.3420. Loss at 120°, 0.0361, 0.333.

Calc. for $C_{12}H_6S_{10}K_{10}O_{20} \cdot 8H_2O$: H_2O , 9.11. Found: H_2O , 9.85, 9.74.

Subs. dried at 120°, 0.3340, 0.3318, 0.1325, 0.1048, 0.1666, 0.1921, 0.1974; CO_2 , 0.1271, 0.1248; H_2O , 0.0199, 0.0227; $BaSO_4$, 0.2014, 0.1606, 0.2605; K_2SO_4 , 0.1156, 0.1169.

Calc. for $C_{12}H_6S_{10}K_{10}O_{20}$: C, 10.03, H, 0.42, S, 22.28, K, 27.20. Found: C, 10.40, 10.26, H, 0.66, 0.76, S, 20.87, 21.00, 21.47, K, 27.02, 26.59.

These determinations of sulfur leave much to be desired, and this is undoubtedly due to the great difficulty with which the compound is decomposed in the Carius tube. If the heating was carried on for but one night as usual, only about 18% of S was found. To get the results given above it was necessary to heat the tubes for 36 hours, and it may well be that even then a portion of the substance had escaped decomposition. Reasons have been given in the introduction for thinking that this is the α -water addition product of potassium *o*-euthiochronate containing one molecule of water, perhaps of crystallization, $[C_6(SO_2K)_5(OH)_2]_2O \cdot H_2O$.

Properties.—It forms white plates, slightly soluble in cold, freely in hot water, from which it crystallizes finely, insoluble in alcohol. Strong nitric acid has no apparent action on it. Barium chloride gives with its solution a white precipitate, which is soluble in hydrochloric acid. Silver nitrate, or lead acetate also gives a white precipitate. With the small amount of material at our disposal we did not succeed in obtaining any of these precipitates free from potassium. Ferric chloride gives with a solution of the salt a yellow color somewhat darker than its own. An attempt to make the sulfochloride was unsuccessful. Heating the salt with hydrochloric acid in a sealed tube gave no action below 150°, and at this temperature the substance was charred completely. Sodium hydroxide had no action on the salt, even when a strong solution was boiled with it.

Action of Dimethylamine on Tetrabromo-*o*-quinone.—Five grams of tetra-bromo-*o*-quinone were dissolved in 50 cc. of ether, and after cooling the solution with ice, dimethylamine was passed into it, as long as black crystals separated. The same result was obtained when alcohol, or chloroform, was used as the solvent. The black product was recrystallized from benzene, or chloroform, and dried rapidly *in vacuo*.

Calc. for $C_6Br_4O_2(NH(CH_3)_2)_2$: Br, 62.24. Found: Br, 62.88, 63.40.

These results—the best we obtained—are as good as could be expected, because the substance decomposes on solution forming a red product, and giving off the odor of dimethylamine, and it is also converted into a tar by standing dry for some time even *in vacuo*.

Properties.—Black crystals, which decompose between 115° and 125°, the temperature being so much affected by the conditions of heating that no definite point can be given. On standing in the air or over sulfuric acid it is converted into a tar—a change which takes place rapidly, if the substance has not been washed and recrystallized, and goes on slowly

even under the most favorable conditions. It is soluble in alcohol, acetone, chloroform, benzene, or toluene; slightly soluble in ether; essentially insoluble in water, or naphtha. The solution of the compound is always attended with decomposition shown by the appearance of a red substance and of a tar if the solution is allowed to stand for some time.

Similar black crystals were obtained, when alcoholic solutions of dimethylamine and tetrachloro-*o*-quinone were mixed after having been cooled with ice. An analysis after washing with water gave 39.50% Cl instead of the 42.27% Cl required, if one molecule of the quinone had combined with two of the amine. Owing to the instability of the substance, which prevented purification, a better result could not be expected. On standing dry or being dissolved with a view to purifying, it was converted into a tar, and it decomposed on heating. It seems, therefore, to be a little less stable even than the corresponding bromine compound, and is less soluble than this, since it is only slightly soluble in alcohol, or acetone, and nearly insoluble in chloroform, tetrachloride of carbon, disulfide of carbon, benzene, or toluene, but soluble in ether.

CAMBRIDGE, MASS.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

NOTE ON TETRABROMO-*o*-PHENYLENEDIACETAMID.

BY C. LORING JACKSON AND SYDNEY A. BEGGS.¹

Received January 6, 1916.

In some earlier work² in this laboratory an attempt was made to prepare tetrabromo-*o*-phenylenediamine by the action of bromine on the free base, but the only products were amorphous red substances, which were supposed to be formed by the action of bromine on the amino groups. Accordingly in taking up the work again we protected these groups by the introduction of acetyl, and had no difficulty in obtaining tetrabromo-*o*-phenylenediacetamid (not melting below 280°) by the direct action of bromine on dibromo-*o*-phenylenediacetamid. When we attempted to remove the acetyls from this substance with sulfuric acid, we found that a molecule of water was removed instead. This was not unexpected, but we had hoped that some other saponifying agent might be found, which would yield the free diamine. With this end in view we tried a solution of sodium hydroxide in an open vessel, and alcoholic ammonia in a sealed tube, but each gave the same result as the sulfuric acid, that is, a compound melting at 265–266° (uncorr.), which without doubt is the acet

¹ The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by Sydney Adams Beggs.

² Jackson, Russe, *Am. Chem. J.*, 35, 148 (1906).

derivative of the 2-methyltetrabromobenzimidazol of Baczynski and Niementowski.¹

In preparing the dibromo-*o*-phenylenediacetamid on one occasion, when the action was carried on in the cold, we obtained instead the *o*-aminodibromophenylacetamid which melted at 189° (uncorr.).

Experimental.

4,6-Dibromo-2-nitroaniline prepared according to Russe and one of us² was warmed on the steam bath with an excess of tin and strong hydrochloric acid, until the yellow color had gone; and after it had cooled, and an excess of sodium hydroxide had been added, it was extracted with ether, which gave a yield of about 78% of the theoretical, whereas Russe by distillation with steam obtained only a little over 5%. This process, however, had the advantage of yielding a pure product, whereas ours was still impure.

2-Amino-4,6-dibromoacetanilid, $C_6H_3Br_2NH_2NHC_2H_5O$.—When the dibromo-*o*-phenylenediamine was mixed with a slight excess of acetic anhydride, a considerable amount of heat was given off, and the mixture solidified. After it had been allowed to stand for 10 minutes, the product was treated with water, and warmed, until the excess of acetic anhydride had been destroyed. The crude acetamid from 6.5 g. of the amine weighed 7 g. It was purified by frequent crystallization from dilute alcohol, until it showed the constant melting point 189° (uncorr.).

Subs., 0.1479. AgBr, 0.1797. Calc. for $C_6H_3Br_2NH_2NHC_2H_5O$: Br, 51.94. Found: Br, 51.71.

Properties.—White needles from dilute alcohol melting at 189° (uncorr.). It is soluble in alcohol, ether, chloroform, tetrachloride of carbon, disulfide of carbon, benzene, or toluene; essentially insoluble in naphtha.

Tetrabromo-*o*-phenylenediacetamid, $C_6Br_4(NHC_2H_5O)_2$.—The dibromodiacetamid used in this work was made by the method of Russe and one of us,³ warming the amine with acetic anhydride for 15 minutes. We found that it could be crystallized either from dilute alcohol, or dilute acetic acid. Ten grams of this substance were dissolved in glacial acetic acid, and boiled under a return condenser with 10 g. of bromine in the sunlight. During the first 8 hours of boiling there was no apparent action, but when, after standing overnight, the mixture was heated on the following day, hydrobromic acid was given off, showing that the reaction had started. As the boiling went on, more hydrobromic acid came off, and a white solid was deposited; and when after 11 hours no more gas appeared, the product was filtered out, and crystallized three times from dilute alcohol.

Subs., 0.1113. AgBr, 0.1655. Calc. for $C_6Br_4(NHC_2H_5O)_2$: Br, 62.98. Found: Br, 63.30.

¹ *Zentrbl.*, 1902, II, 940.

² *Am. Chem. J.*, 35, 149 (1906).

³ *Ibid.*, 35, 152 (1906).

Properties.—White prisms from dilute alcohol, which did not melt even at 280° . It is soluble in alcohol; slightly soluble in ether; essentially insoluble in water, chloroform, acetone, glacial acetic acid, naphtha., or benzene.

2-Methyltetrabromobenzacetimidazol, C_6Br_4  $COCH_3$, CCH_3 . — One gram

of tetrabromo-*o*-phenylenediacetamid was boiled under a return condenser with equal parts of sulfuric acid and water for 4 hours, when upon adding sodium hydroxide to the solution a precipitate was thrown down, which after 3 crystallizations from dilute alcohol melted constant at $265-266^{\circ}$ (uncorr.). The same product was obtained, when 0.5 g. of the diacetamid was heated for 4 hours in a sealed tube with alcoholic ammonia. After evaporating off the solvent, and recrystallization from dilute alcohol, the melting point was 265° (uncorr.). Upon boiling some of the diacetamid for 2 hours with a solution of sodium hydroxide, diluting with water, and extracting with ether, a product was obtained, whose melting point in the crude state showed it was identical with the other two.

Subs., 0.1077, 0.1207. AgBr, 0.1646, 0.1848. Calc. for $C_{10}H_4Br_4N_2O$: Br, 65.30. Found: Br, 65.03, 65.18.

Properties.—White crystals melting at $265-266^{\circ}$ (uncorr.). It is soluble in all the common organic solvents, but insoluble in water.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF APPLIED CHEMISTRY, ENGINEERING COLLEGE, IMPERIAL UNIVERSITY OF JAPAN.]

THE ESSENTIAL OIL OF SUGI (*Cryptomeria japonica*) LEAVES.

By So UCHIDA.

Received December 8, 1915.

The Sugi (*Cryptomeria japonica*, Don.) is a coniferous tree, indigenous to Japan, and is extensively cultivated throughout the whole empire as a valuable timber tree. The wood is most widely used and prized as a timber wood and for general woodworking. The stems, leaves and roots contain essential oil. No study, as far as I know, has hitherto been made of the oil contained in the leaves.

The green leaves of Sugi, weighing 87.4 kg., on distillation with steam, yielded 612 g. of volatile oil, which is equivalent to 0.70%. The oil is mobile, brownish yellow in color and has a fresh aromatic odor. When the oil was cooled to -5° for an hour in a mixture of ice and salt, no solid substance separated. A small amount of the oil was distilled in a flask under atmospheric pressure; it began to boil at about 155° and continued to distil until the thermometer reached 350° , the following fractions being obtained: $155-190^{\circ}$ 33%, $190-230^{\circ}$ 4%, $230-270^{\circ}$ 4%, $270-$

310° 28%, 310–350° 23%. When bromine was added drop by drop, the oil combined violently with it, evolving a large amount of heat and changed to a greenish, viscous oil. Two drops of the oil were dissolved in 1 cc. of acetic anhydride and then shaken with a drop of concentrated sulfuric acid. The liquid assumed an intense green color and became very viscous. When a few drops of the oil were added to 2 cc. of concentrated sulfuric acid, the oil dissolved in it, assuming a yellowish brown color, and slowly a small amount of thick reddish brown oil formed on the surface of the liquid. The oil does not give any characteristic color reaction with very dilute ferric chloride solution. It does not reduce ammoniacal silver oxide, and contains neither nitrogen nor sulfur. The oil is completely soluble in the usual organic solvents and furnishes the following constants:

$d_{16}^{16.5}$	0.9217	Acid value.....	1.0
$[\alpha]_D^{16}$ in 10% chloroform soln.	19.29	Ester value.....	6.56
n_D^{20}	1.4895	Ester value after acetylation....	14.35

The total amount of the oil employed for the investigation was 454 g.

Treatment with Sodium Carbonate.—In order to separate any uncombined acids, the oil was three times successively extracted with a 5% solution of sodium carbonate. The combined alkaline liquid of brownish yellow color was shaken with ether four times. The ethereal solution, after evaporating off the ether, was added to the main part of the oil. The alkaline water solution was then acidified with sulfuric acid and extracted thoroughly with ether. The ethereal liquid, thus obtained, was washed with water and dried with anhydrous sodium sulfate. On evaporating off the ether, there remained a yellowish, very viscous oil having an odor of higher fatty acids, but its amount was too small to admit of further examination.

Fractional Distillation of the Oil.—The oil, shaken with dilute sodium carbonate solution, was washed with water successively until the wash water was neutral to litmus and then dried with anhydrous sodium sulfate. It was subsequently subjected to fractional distillation under 15 mm. pressure, a current of carbon dioxide being passed into the liquid to insure regular ebullition, and was resolved into the following three fractions:

I.....	50–100°	31%
II.....	100–180°	42%
III.....	180–200°	17%

Identification of α -Pinene.—Fraction I (b. p. 50–100° under 15 mm. pressure). This fraction, representing in fact nearly one-third of the whole of the oil employed, was a mobile, colorless liquid and had a somewhat lemon-like odor. When heated with a small piece of sodium, it was found to be practically unacted on. The oil, after purifying by repeated distillation over sodium under 50 mm. pressure, was finally dis-

tilled under atmospheric pressure and was resolved into the following three fractions:

(a), 158–163°; (b), 163–168°; (c), 168–172°.

Fraction 158–163°. The greatest portion of this fraction, on redistillation, boiled at 161–162°. It was colorless and mobile and possessed a turpentine-like odor. It had a specific gravity of 0.8567 at 15.5/15.5 and $n_D^{20} = 1.4666$. It is optically active and rotates the plane of polarization to the right in a 100 mm. tube by $2^\circ 30'$.

Preparation of Nitrosochloride.—The nitrosochloride was made by a slightly modified method of Wallach.¹ A white, lamellar, crystalline substance separated, which was collected, washed with cold alcohol and finally purified by precipitating with methyl alcohol from its chloroform solution. The crystals, thus purified, melted at 103–104° to a brownish black liquid.

Preparation of Nitropiperidine and Nitrolbenzylamine.—When the nitrosochloride was heated on the water bath with an excess of piperidine in alcoholic solution, a vigorous action occurred resulting in the formation of nitropiperide, and the liquid assumed a pale yellowish green color. After cooling, sufficient water was added and an oily substance of yellowish brown color precipitated, which solidified to a crystalline mass on standing overnight. When purified by several recrystallizations from a mixture of ether and alcohol, it melted constant at 118–119°.

A nitrolbenzylamine was also prepared from the nitrosochloride by a similar method. After recrystallization, it melted constant at 122–123°. Thus the identification of this fraction with α -pinene was established.

Fraction 163–168°. This has a density $d_{15.5}^{15.5} = 0.8570$ and $[\alpha]_D^{15} = 17.37^\circ$ in a 100 mm. tube. The index of refraction is $n_D^{15} = 1.4679$. It was a colorless, mobile liquid, having a pleasant odor. This fraction was specially tested for β -pinene but with a negative result.

Fraction 168–172°. This fraction was a colorless, mobile liquid having a pleasant odor and was relatively small in amount. The liquid when examined in a tube 100 mm. long, at 20°, produced a rotation 24.81° to the right. A density determination gave $d_{15.5}^{15.5} = 0.8778$ and the index of refraction was $n_D^{20} = 1.4736$.

Preparation of Dibromide.—To detect the presence of limonene or dipentene in this fraction, bromine was added drop by drop in a well-cooled solution of the fraction in glacial acetic acid. The color disappeared at first and did not become permanent until two atoms of bromine had been added for every molecule of the compound. Since nothing had separated from the solution even after two days, the product was precipitated by the addition of water and taken up with ether. The ethereal

¹ *Ann.*, 245, 241 (1888).

solution was washed with solution of sodium carbonate and afterwards with water and dried with anhydrous sodium sulfate. After evaporating off the ether, the residue was kept in a vacuum over paraffin for several weeks. Bromine was estimated by Carius's method.

0.2822 g. gave 0.3664 g. AgBr. Br = 55.25%. $C_{10}H_{16}Br_2$ requires Br = 54.00%.

Thus the fraction was dibromic and the absence of limonene or dipentene was confirmed. A careful search was also made for terpinene, sylvestrene, phellandrene and cineol in this fraction, but none of them was detected.

The presence of α -pinene in these preceding two fractions was also confirmed by means of the nitrosochloride, nitrolpiperidine and nitrolbenzylamine. The low-boiling fraction of Sugi leaves oil, therefore, consists chiefly of α -pinene.

Hydrolysis of Fraction II.—In order to hydrolyze the ester, Fraction II, boiling between 100 and 180° under 15 mm. pressure, was boiled for three hours with alcoholic potash in a flask connected with a reflux condenser. After the greater part of alcohol had been removed by distillation, the liquid was transferred to a separating funnel and a sufficient quantity of sodium chloride solution was added to effect the separation of the oil. The aqueous alkaline liquid separated from the oil was shaken with successive portions of ether to remove the last trace of oil. The aqueous alkaline liquid thus extracted with ether was set aside for the examination of the acids. The ethereal extract was mixed with the separated oil, washed with water four times successively and dried with anhydrous sodium sulfate. After distilling off the ether, the oil was fractionally distilled twice under atmospheric pressure and was resolved into the following four fractions:

(a), 195–235°; (b), 235–280°; (c), 280–310°; (d), 310–330°.

Fraction 195–235°. This fraction was relatively small in amount, representing 7% of the whole of the oil investigated and was freely soluble in 70% alcohol. It was distilled under atmospheric pressure, coming over mainly at 212–214°. The two chief fractions, boiling at 185–205° and 205–220°, were collected.

Identification of Dipentene.—Fraction 185–205°, which evidently contained terpenes, was distilled over metallic sodium under atmospheric pressure and the following three fractions were obtained: 168–172°, 172–175°, 175–178°, weighing 2.28 g., 2.35 g., and 1.90 g., respectively.

To detect the presence of limonene or dipentene in these fractions, bromine was added drop by drop to their well-cooled solutions in glacial acetic acid until the color of bromine remained permanent.

Fraction.	Weight of oil.	Bromine used.	Percentage of Br.
168–172°	2.28 g.	1.08 cc. = 3.44 g.	151%
172–175°	2.31 g.	1.04 cc. = 3.31 g.	143%
175–178°	1.90 g.	0.97 cc. = 3.09 g.	163%
Dibromic $C_{10}H_{16}$ requires 117.7% Br. Tetrabromic $C_{10}H_{16}$ requires 235.3% Br.			

It is obvious from the result of the experiments that these fractions contain a considerable amount of a tetrabromic terpene. After standing for 4 days, they became brownish black liquids and only Fraction 175–178° deposited an exceedingly small amount of white crystals. These were collected, drained on a porous tile and recrystallized three times from acetic ether. The product melted at 123–124°. Thus the presence of dipentene in this fraction was confirmed.

Alcohol.—Fraction 205–220°, obtained as above described, was then redistilled. The main portion passed over between 210 and 215°, and especially between the limits 212–214°. This fraction (212–214°) was a faint yellow, mobile liquid possessing a powerful fresh odor recalling that of camphor and peppermint at the same time. When cooled to –15°, it did not show any tendency to crystallize, even after a lapse of several hours.

0.2557 g. gave 0.7348 CO ₂ and 0.2792 H ₂ O.....	C = 78.35	H = 12.13
C ₁₀ H ₁₈ O requires.....	C = 77.85	H = 11.77

0.5727 g. dissolved in 19.076 g. benzene caused a depression of the freezing point of 0.923°. Hence the molecular weight = 162.7. C₁₀H₁₈O requires 154.1.

It does not reduce ammoniacal silver oxide. It has a density $d_{15}^{18} = 0.9414$ and produced a rotation $[\alpha]_D = +56.07^\circ$ in 8.98% chloroform solution. The refractive index is $n_D^{18} = 1.4832$, M. R. = 46.80.

Acetylation Experiment.—The oil was boiled for two hours with acetic acid anhydride in the presence of anhydrous sodium acetate, and then a sufficient quantity of water was added and it was heated for two hours on a water bath. The product was repeatedly extracted with ether and the ethereal solution was washed first with dilute sodium carbonate solution and then with water and dried with anhydrous sodium sulfate. On evaporating off the ether, a pale yellow, mobile liquid having an aromatic odor was obtained.

The acetylated oil was saponified with 0.5 *N* alcoholic potash and the excess of potassium hydroxide was titrated with sulfuric acid. 1.5016 g. acetylated oil required for saponification 0.2146 g. KOH. For an acetic ester of the formulae C₁₀H₁₇O.COCH₃, 0.4295 g. KOH would be required. From this result it will be seen that this alcohol cannot be entirely converted into its acetic ester, perhaps due to the partial decomposition during the operation as in the case of linalool.

Oxidation with Bichromate and Permanganate.—This fraction was then oxidized with chromic acid mixture and after reducing the excess of bichromate, the product was distilled with steam. The distillate was made alkaline by potassium carbonate and extracted thoroughly with ether and the ethereal liquid was washed, dried and evaporated. The brownish yellow, mobile oil, thus obtained, possessed a high aromatic

odor and did not reduce ammoniacal silver oxide. On combustion, it was found to consist of $C = 70.41\%$, $H = 12.44\%$, $O = 17.15\%$.

Oxidations with permanganate at ordinary and at ice-cold temperature were also made, but no characterized products were obtained.

This alcohol, though existing in small amount, has evidently a considerable influence on the odor of the original oil and it can be regarded as the chief odorous constituent of the oil.

Sesquiterpenes.—Fraction $235-280^\circ$. This fraction, representing about 22% of the oil employed, was a yellowish green, viscous oil and was sparingly soluble in 70% alcohol. It was found to give only a slight action with sodium and hence consisted almost entirely of hydrocarbons. The fraction was purified by repeated distillation over sodium under reduced pressure, until the metal remained bright through the whole distillation, and it was finally distilled over sodium under atmospheric pressure. Thus purified, it passed over chiefly between $260-270^\circ$ and smaller fractions were also collected at $250-260^\circ$ and $270-280^\circ$. Most of the oil distilled over between 266 and 268° . Fraction $260-270^\circ$ was, therefore, redistilled and a fraction boiling at $266-268^\circ$ was collected. On combustion, it gave the following figures:

0.3497 g. gave 1.1233 CO_2 and 0.3593 H_2O	$C = 87.60$	$H = 11.42$
$C_{15}H_{24}$ requires.....	$C = 88.16$	$H = 11.84$

0.3476 g. substance in 18.523 g. of benzene caused a depression of the freezing point of 0.449° . Hence the molecular weight is 209.0. $C_{15}H_{24}$ requires 204.2.

This fraction, therefore, consists of a sesquiterpene. It furnished the following constants:

$$d_{15.5}^{15.5} = 0.9335, d_{22.8}^{22.8} = 0.9245.$$

$$[\alpha]_D = +15.19^\circ \text{ in a } 6.08\% \text{ chloroform solution. } n_D^{22.8} = 1.5041.$$

The molecular refractive energy of the compound calculated by means of the formulae $n^2 - 1/n^2 + 2.M/d$ is, therefore, 65.3. The calculated number for $C_{15}H_{24}$ with two double linkings is 66.15. This evidence of the presence of two pairs of "doubly linked" carbon atoms is borne out by the analysis of the hydrochloride described below.

The liquid was viscous and almost colorless and possessed a weak hay-like odor. When a few drops of this fraction were dissolved in a few cc. of acetic acid anhydride and shaken with one drop of concentrated sulfuric acid, the liquid assumed a yellowish green color which at once became green, then blue and finally turned to a deep indigo color.

Action of Hydrogen Chloride.—Dry hydrogen chloride was passed into a well-cooled solution of Fraction $266-268^\circ$ in two times its volume of ether. The gas was readily absorbed and the liquid finally became brown. After saturating the liquid with hydrogen chloride, it was corked tightly and allowed to remain overnight, when the liquid turned to violet-black. This, after being washed with ice-cold water four times, was dried with

anhydrous sodium sulfate. On evaporating off the ether under reduced pressure, a brownish black oil of very viscous nature was left, which was allowed to remain for several weeks in a vacuum over paraffin and calcium chloride. The oil, thus obtained, on being cooled to -20° , became more viscous, but did not show any tendency to crystallize even after a lapse of three hours. A chlorine determination was made by Carius's method.

0.4937 g. gave 0.4760 AgCl, Cl = 23.85%; $C_{18}H_{34}.2HCl$ requires Cl = 25.59%.

Though a small discrepancy is observed between the experimental result and the theoretical value for chlorine, owing to the unstable nature of the hydrochloride, it is clear that the sesquiterpene has two double linkings. To obtain a crystalline derivative of this sesquiterpene, the preparation of a nitrosochloride, a nitrosite, a bromide, a nitrosate and a hydrate were carefully tried by the well-known methods but the results were unsatisfactory.

Identification of Cadinene.—Fraction $270-280^{\circ}$ obtained by the redistillation of Fraction $235-280^{\circ}$ over sodium was relatively small in amount. In order to test for the presence of cadinene, as it is often found in essential oils, this fraction was redistilled and a fraction boiling between $272-275^{\circ}$ was collected. A hydrochloride of this fraction was prepared exactly as above described. The resulting brownish black oil of very viscous nature was kept in a vacuum over paraffin and calcium chloride for several weeks when exceedingly small quantities of minute needle crystals separated from the liquid. These were collected, drained on a porous tile and crystallized from acetic ether. The white, lustrous, needle-shaped crystals, thus obtained, melted constantly at $117-118^{\circ}$ to a reddish liquid suffering almost no decomposition. A chlorine determination by the Carius method gave the following result:

0.0375 g. gave 0.0385 AgCl, Cl = 25.40%; $C_{18}H_{34}.2HCl$ requires Cl = 25.59%.

A mixture of these crystals and cadinene hydrochloride did not show any depression of the melting point, confirming the presence of cadinene in this fraction.

Sesquiterpene Alcohol.—Fraction $280-310^{\circ}$. This fraction, representing about 10% of the oil employed, had a very beautiful deep blue color and was sparingly soluble in 70% alcohol. On successive redistillation under atmospheric pressure, the greater part of the oil passed over between $280-290^{\circ}$, mainly at $284-286^{\circ}$. Fraction $284-286^{\circ}$, collected during the distillation, was a viscous liquid, having a beautiful deep blue color and a weak characteristic odor. On cooling to -10° , it became more viscous but did not show any tendency to crystallize even after the lapse of several hours. This liquid, when dissolved in glacial acetic acid and treated with a drop of concentrated sulfuric acid, yielded a green color which turned to blue at once and finally to deep indigo. It has a density $d_{15.5}^{15.5} = 0.9623$; $[\alpha]_D^{15} = 16.76^{\circ}$ in a 5% chloroform solution and $n_D^{22.8} = 1.5048$.

0.2251 g. gave 0.6717 CO ₂ and 0.2319 H ₂ O.....	C = 81.39	H = 11.45
0.2162 g. gave 0.6448 CO ₂ and 0.2274 H ₂ O.....	C = 81.32	H = 11.69
0.2678 g. gave 0.7986 CO ₂ and 0.2919 H ₂ O.....	C = 81.34	H = 12.11
C ₁₅ H ₂₆ O requires.....	C = 81.01	H = 11.79

0.3625 g. dissolved in 19.08 g. benzene caused a depression of the freezing point of 0.435°. Therefore, the molecular weight = 218.0. C₁₅H₂₆O requires 222.2.

This fraction, therefore, consists of a sesquiterpene alcohol. Several essential oils are known to afford high boiling fractions of a deep blue color for which the name "Azulene" had been proposed by Piesse and "Coerulein" by Gladstone. The compound was recently investigated by A. E. Sherndal¹ and found to be a hydrocarbon, C₁₅H₁₈, having such a striking color intensity that 0.064 g. dissolved in a liter of benzene matches an ammoniacal solution of copper sulfate containing 0.24 g. CuSO₄ to the liter in depth of color. The deep blue color of this fraction is in all probability due to the presence of a trace of a blue hydrocarbon, "Azulene," while a sesquiterpene alcohol makes up the bulk of the oil.

Fraction 310–330°. This fraction, weighing 5 g. or 1% of the whole of the oil used, had a deep blue color and was a very viscous oil when first distilled. But after a time it deposited a considerable amount of white, needle-like crystals which were collected, washed with glacial acetic acid and recrystallized from acetic ether. It melted accurately at 61° and was confirmed to be identical with a new diterpene consisting of the next fraction and will further be discussed later. The oil after separating the crystals was of deep blue color and very viscous. It gave the same color reaction as that of the preceding fraction. Thus, this fraction is apparently a mixture of the preceding and the following fraction.

A New Diterpene.—Fraction III. Fraction III (180–200° under 15 mm. pressure), obtained by the fractional distillation of the oil treated with sodium carbonate solution, was 75 g. or 16.5% of the whole of the oil used. When first distilled, it was an oil of very viscous nature, possessing a yellow color, but when cooled to the room temperature it solidified to a crystalline hard mass. To separate any adhering oily substance, the total mass was poured into glacial acetic acid, drained on a porous tile, washed with cold alcohol and finally purified by recrystallization from acetic ether, from which it separated in the form of white, glistening, odorless, stellated needles. Thus purified, it melted at 61°.

0.3902 g. gave 1.2571 CO ₂ and 0.4137 H ₂ O.....	C = 87.86	H = 11.78
0.2530 g. gave 0.8143 CO ₂ and 0.2704 H ₂ O.....	C = 87.80	H = 11.87
0.3970 g. gave 1.2789 CO ₂ and 0.4294 H ₂ O.....	C = 87.86	H = 12.01
C ₂₀ H ₃₂ requires.....	C = 88.16	H = 11.84

Determinations of its molecular weight, using benzene as the solvent.

I, 0.6845 g., and II, 1.2235 g., in 20.250 g. benzene gave 0.637° and 1.150° depression, = M. W. 265; 263. C₂₀H₃₂ requires 272.

¹ THIS JOURNAL, 37, 167, 1537 (1915).

This substance, therefore, is a diterpene. It has a very high boiling point and boils, in fact, at 198° under 15 mm. pressure and at 345° under atmospheric pressure without any decomposition. It is laevorotatory, $[\alpha]_D^{20} = -34.32^{\circ}$ in a 4.69% chloroform solution. It is readily soluble in ether, chloroform, benzene and petroleum ether; soluble in hot acetic ether; difficultly soluble in cold acetic ether and hot alcohol and insoluble in glacial acetic ether and in cold alcohol. Thus, it is most convenient to wash with glacial acetic acid to separate any adhering oil from the crystals and to use acetic ether for recrystallization. A few drops of an ether solution of iodine were added to a solution of this diterpene in the same solvent but the color of iodine remained permanent. This indicates this crystalline diterpene to be a saturated compound. Also, this diterpene is difficultly combustible.

Action of Bromine.—On adding bromine drop by drop to this diterpene directly, no violent reaction occurred and a reddish brown resinous substance was formed which it was impossible to crystallize by any means.

Action of Sulfuric Acid.—The crystalline diterpene was added to concentrated sulfuric acid, in which it dissolved at first, assuming a yellowish orange color and a reddish orange oily substance slowly formed on the surface of the liquid. After standing overnight, the liquid was added drop by drop to a sufficient quantity of water, care being taken not to raise the temperature above 30° during the operation (otherwise, sulfuric acid oxidizes the oil with evolution of sulfur dioxide), when a yellowish orange oily substance precipitated which was taken up with ether. The ethereal solution was washed with cold water until it gave no acid reaction to litmus and was then dried with anhydrous sodium sulfate. On evaporating off the solvent carefully, a pale yellow, viscous oil of somewhat petroleum-like odor was left which did not crystallize even after cooling to -15° for several hours. The oil thus obtained was allowed to remain for several weeks in a vacuum desiccator filled with paraffin to eliminate the last trace of ether. After the lapse of that time, the oil became very viscous, in fact, a semi-resinous substance. Suspecting this substance to be a sulfonic derivative of the diterpene, a determination of sulfur was made but the substance was found not to contain sulfur.

Fuming sulfuric acid reacts violently with this diterpene evolving a large amount of heat and the substance was charred.

Action of Hydrogen Chloride.—On passing dry hydrogen chloride into a well-cooled solution of this diterpene in ether, a large amount of white crystals separated and the liquid assumed a faint yellow color. The compound, after separating from the liquid, was washed with ether and recrystallized from acetic ether, from which it separated as fine, white needles having a radial aggregation. The crystals, thus purified, melted at $211-212^{\circ}$. When pressed with a glass rod, the substance gives a soft

elastic feeling. It is difficultly soluble in ether and in cold acetic ester but soluble in hot acetic ester and in phenol. The crystals, when melted, sublime and float in the air as light feathers.

0.1967 g. gave 0.6342 CO_2 and 0.2111 H_2O C = 87.90 H = 11.91
 $\text{C}_{20}\text{H}_{32}$ requires..... C = 88.15 H = 11.85

I, 0.0863 g., and II, 0.0528 g., in 25.75 and 20.34 g. phenol gave a depression of 0.090 and 0.070°. M. W. found, 276 and 275. $\text{C}_{20}\text{H}_{32}$ requires 272.

This substance is, therefore, an isomer of the crystalline diterpene above described.

For the diterpene isolated by the author from Sugi leaves oil the clear evidence of its chemical individuality justifies me, I think, in proposing for it the designation of " α -Cryptomerene" in consideration of its botanical source. The name " β -Cryptomerene" is also suggested for the crystals precipitated from the ethereal solution of " α -Cryptomerene" by hydrogen chloride. For the sake of clearness, all known diterpenes¹ which have been investigated, and their properties will be given in the table below.

Acids Obtained by the Hydrolysis of the Oil.

The alkaline aqueous liquid, separated from the hydrolyzed oil and completely extracted with ether, as previously described, was acidified with sulfuric acid and distilled with steam. The first portion of the distillate was slightly turbid but it became clear after a time and about 600 cc. of the distillate were collected. A few drops of brownish oily substance floated on the surface of the distillate. The entire acid liquid was made alkaline with sodium carbonate and shaken four times successively with ether. The ethereal liquid was washed with a little water four times and dried with anhydrous sodium sulfate. On evaporating off the solvent, there remained an exceedingly small amount of highly aromatic, semi-solid substance of brown color. It gives no reaction of phenol and is insoluble in a cold solution of potassium hydroxide but readily dissolves on warming. After keeping in a vacuum over paraffin, it was analyzed:

0.0647 g. gave 0.1870 CO_2 and 0.0627 H_2O C = 78.83 H = 10.76
 $\text{C}_{20}\text{H}_{32}\text{O}_2$ requires..... C = 78.86 H = 10.60

This substance, to which we assign the provisional formula $\text{C}_{20}\text{H}_{32}\text{O}_2$, is evidently a lactone.

The alkaline solution, from which the lactone had been separated, was evaporated to a small bulk, strongly acidified with sulfuric acid and extracted several times with ether. The ethereal solution was washed four times with a little water, dried and evaporated. The slightly colored oily residue, thus obtained, was viscous in nature and possessed a pungent odor resembling that of acetic acid. It was difficultly soluble in water and crystallized at 11°.

¹ Two or three diterpenes, not included in this list, are mentioned in the formula register.—EDITOR.

Author.	Designation.	Mode of formation or occurrence.	B. p.	M. p.	Sp. gr.	
Dewille	Colophene	By the action of concentrated sulfuric acid or phosphoric acid anhydride on turpentine oil	318-320°	Unites with HCl
Berthelot	Metatercenthene	By heating turpentine oil at 300°.	Above 360°	0.931	Absorbs HCl, laevorotatory
Hell and Stürcke	Diclene	By the action of phosphoric acid anhydride on wormseed oil	328-333°	
Lafont	Diterpene	By the action of formic acid on limonene	212-215° (40 mm.)	0.9409	$\alpha_D^{20} = +0$ Combines with HCl forming a semi-solid matter, $C_{26}H_{42}$.HCl.
Schmidt	Paracajepitene	By heating cajeput oil with phosphoric acid anhydride	310-316°	Absorbs HCl
Berkenheim	Diterpene from menthone	By heating menthone with phosphoric acid anhydride	320-325°	0.9535	Combines with HCl, forming a crystal, $C_{26}H_{42}$.HCl, m. p. = 129-131°
Semmler	α -Camphorene	From the high boiling fraction of camphor oil	177-178° (6 mm.)	0.8870	Combines with HCl, forming a crystal, $C_{26}H_{42}$.HCl, m. p. = 129-131°
Semmler	β -Camphorene	From the high boiling fraction of camphor oil	170-180° (6 mm.)	0.930	$[\alpha]_D^{20} = 34.22^\circ$ in a 4.7% chloroform solution. A saturated compound
Uchida	α -Cryptomerene	From the high boiling fraction of oil of cryptomeria japonica leaves	At 345° (760 mm.)	61°	White, needle-crystal, radial aggregation
Uchida	β -Cryptomerene	By passing hydrogen chloride to a solution of α -cryptomerene in ether	212°	Soft, white, needle-crystal, radial aggregation Causes a vigorous sublimation at the temperature of melting point. A saturated compound

Titration of the Acid.—A decinormal alcoholic potash was run into a solution of the acid in the same solvent, phenolphthalein being used as indicator. 0.2736 g. acid required for neutralization 104.8 mg. KOH. For a monobasic acid of the formula $C_8H_{16}O_2$, 106.5 g. KOH would be required. The silver salt, prepared from the potassium salt, gave the following number on analysis:

0.1045 g. gave on ignition 0.0462 Ag..... Ag = 44.21%
 $C_8H_{16}O_2Ag$ requires..... Ag = 43.16%

The small amount of the acid did not permit further investigation but its general properties and the result of analysis served to confirm the acid to be caprylic acid. It may also be noted that the ester of this alcohol was present in relatively small amount in the oil and the greater part of the alcohol exists in the oil in a free state.

Summary.

From the preceding details it will be seen that this essential oil of Sugi (*Cryptomeria japonica*) leaves contains the following substances:

1. *d*- α -Pinene.
2. Dipentene.
3. An alcohol ($C_{10}H_{18}O$, b. p. = 212–214°, $d_{15} = 0.9414$, $n_D^{22.8} = 1.4832$).
4. Cadinene.
5. A sesquiterpene with two double linkings ($C_{15}H_{24}$, b. p. = 266–268°, $d_{15} = 0.9335$, $n_D^{22.8} = 1.5041$, $[\alpha]_D = +15.19^\circ$ in a 6.08% chloroform solution).
6. A sesquiterpene alcohol ($C_{15}H_{26}O$, b. p. = 284–286°, $d_{15.5} = 0.9623$, $n_D^{22.8} = 1.5048$, $[\alpha]_D^{15} = +16.76^\circ$ in a 5% chloroform solution).
7. A new diterpene ($C_{20}H_{32}$, b. p. = 345°, b. p.₁₅ = 198, $[\alpha]_D = -34.22^\circ$ in a 4.67% chloroform solution) for which the author proposed the name " α -Cryptomerene."
8. A lactone ($C_{20}H_{32}O_2$).
9. Caprylic acid in combination with the alcohol.
10. Higher fatty acids in a free state.
11. A blue oil, "Azulene."

The relative proportion of the above constituents is approximately as follows:

The terpenes, consisting chiefly of *d*- α -pinene with a small quantity of dipentene, represented 34%. The amount of two sesquiterpenes was about 30%, the sesquiterpene of the boiling point 266–268° above mentioned more highly predominating than cadinene. The alcohol represented about 4.5%, and was present partly in the uncombined state and partly as caprylic ester, the former highly predominating. " α -Cryptomerene" represented about 18% of the oil. The amount of sesquiterpene alcohol was about 12%, and finally the amounts of the

lactone, the free fatty acids and a blue oil "Azulene" were exceedingly small.

TOKYO, JAPAN.

[CONTRIBUTION FROM THE DEPARTMENT OF APPLIED CHEMISTRY, ENGINEERING COLLEGE, IMPERIAL UNIVERSITY OF JAPAN.]

ESSENTIAL OIL OF FORMOSAN HINOKI (*Chamaecyparis obtusa*, S. et Z.) WOOD.

By SO UCHIDA.

Received December 8, 1915.

The Hinoki tree (*Chamaecyparis obtusa*, S. et Z.), which is extensively grown in Japan, furnishes a valuable timber wood of superior quality and is likewise prized for the manifold uses to which the wood is well adapted. In the mountain districts (5000-7000 ft.) of Formosa, Hinoki trees thrive most wonderfully, forming a splendid virgin forest. The present paper is concerned with the results obtained in experiments on the composition of Formosan Hinoki wood oil. A sample of the crude oil obtained by the dry distillation of wood was forwarded in 1912 from the Forest office of Arisan Mountains, Formosa. The yield of the crude oil was reported to be 2.4% of the wood. On examination of the sample, it was a reddish brown, mobile liquid possessing a woody and empyreumatic smell and contained some tarry matter.

Rectification of the Crude Oil.—A quantity of the crude oil weighing 780 g. was first rectified by distillation with steam and 700 g. of the rectified oil were obtained which amounted to 89.9% of the crude oil or 2.16% of the weight of wood. The quantity of the distilled water used in rectification was 8 l. The oil thus obtained was mobile, lemon-yellow in color and possessed a Hinoki wood odor. To remove the pyrogenous acids which it still contained, it was subsequently treated with dilute sodium carbonate solution, washed with water and dried with anhydrous sodium sulfate. The oil, thus rectified, has a density $d_{15.5} = 0.8821$; the refractive index $n_D^{18.5} = 1.4990$, and $[\alpha]_D = +50.37^\circ$ in a 10% chloroform solution.

Fractional Distillation of the Oil.—A quantity of the rectified oil weighing 448 g. was distilled fractionally under atmospheric pressure, and began to boil at 157° and continued to distil until the temperature rose to 270° . It was resolved into the following three fractions, a reddish brown, resinous substance amounting to 1.5% of the oil employed remaining in the distilling flask:

I, $157-200^\circ$; II, $200-240^\circ$; III, $240-270^\circ$.

Identification of α -Pinene.—Fraction I ($157-200^\circ$). This fraction, which was by far the largest obtained, representing 68.7% of the whole of the oil used, was mobile and almost colorless. When heated with metallic sodium, it was practically unacted on. The substance was,

therefore, submitted to repeated distillation over sodium under ordinary pressure until the metal remained quite unaltered. The oil, thus purified, passed over chiefly at $155-160^{\circ}$ and a smaller fraction was collected at $160-165^{\circ}$. The chief fraction, when redistilled, boiled mainly at $156-157^{\circ}$. It has a specific gravity $d_{15.5}^{15.5} = 0.8616$; the rotatory power $[\alpha]_D = +44^{\circ} 42'$; and the refractive index $n_D = 1.4662$. It possesses a turpentine-like odor and is mobile and colorless. It was diluted with an equal volume of dry ether, cooled with a mixture of ice and salt and dry hydrogen chloride was passed in it. On evaporating off the diluent, a crop of crystalline substance separated which was collected, drained on a porous tile and recrystallized from alcohol. Since the repeated recrystallization from ethyl alcohol seemed to be insufficient for the purification of the substance, it was finally rectified by sublimation. This product forms white, feathery crystals, smells like camphor and is volatile at ordinary temperature. When pressed, the crystals cling together forming a sticky mass. It melts constantly at $132.5-133.5^{\circ}$ (corr.). The crystals thus rectified by sublimation were again recrystallized three times from alcohol but the melting point of the crystals remained unchanged after each recrystallization.

0.2291 g. gave 0.1892 AgCl. Cl = 20.44%. $C_{10}H_{16}.HCl$ requires Cl = 20.54%.

According to Wallach,¹ pure pinene has the following constants:

B. p. = $155-156^{\circ}$; $d_{20} = 0.858$; $n_D^{21} = 1.46553$.

Flawitzky² gave the physical properties of *d*-pinene obtained from the leaves of *Pinus cembra* as follows:

B. p.₇₇₈ = 156° ; $d_4^{20} = 0.8585$; $[\alpha]_D = +45.04^{\circ}$.

Wallach³ described pinene hydrochloride as follows:

"Reines Pinenhydrochlorid lässt sich so gut wie unzersetzt destillieren und siedet bei 207° bis 208° . Der sehr schwer genau zu bestimmende Schmelzpunkt liegt gegen 125° . Aus Alkohol krystallisiert das Chlorid in gefiederten Krystallen, welche die unangenehme Eigenschaft besitzen, beim Trocknen zu einer sehr klebrigen, an allen Gegenständen sehr haftenden Masse zusammen zu sintern,..... Das schon bei gewöhnlicher Temperatur sehr flüchtige Chlorid verhält sich wie eine völlig gesättigte Verbindung."

According to J. H. Long⁴ pinene hydrochloride melts at 131° and not at 125° .

The physical properties of this fraction coincide fairly well with those of pure pinene as given by Wallach and Flawitzky, and, further, this fraction affords a crystalline monohydrochloric addition product (of all terpenes ever known, pinene is the only one which gives a crystalline monohydrochloric addition product), the properties of which coincide entirely with

¹ Ann., 258, 344.

² J. prakt. Chem., 45, II, 115.

³ Ann., 239, 4.

⁴ THIS JOURNAL, 21, 637 (1899).

those of pinene monohydrochloride described by Wallach. Thus, there is no doubt that this fraction consists of α -pinene. It is worth noting here that pinene hydrochloride melts constantly at 132.5–133.5 (corr.), and neither at 125° (Wallach) nor at 131° (J. H. Long).

Fraction 160–165°. This fraction has a density $d_{13.3}^{15.5} = 0.8642$; the refractive index $n_D^{20} = 1.4672$, and the rotatory power $[\alpha]_D = 46^\circ 27'$. It also furnishes a crystalline monohydrochloride which melts at 132.5–133.5° (corr.). Thus, this fraction also consists chiefly of α -pinene.

Fraction II (200–240°). This fraction was relatively small in amount, representing 8.0% of the oil used, and on redistillation it chiefly separated into fractions boiling above 240° and below 200°. Thus this fraction is apparently a mixture of the preceding and the following fraction with some oxygenated compounds.

Identification of Cadinene.—Fraction III (240–270°). This fraction, amounting to 21.8% of the whole of the oil employed, was a slight yellow, viscous liquid possessing a Hinoki wood odor. It was found to give only a slight action with sodium and hence consisted almost entirely of hydrocarbons which, from their boiling point, seemed to be sesquiterpenes. When purified by repeated distillation over sodium under ordinary pressure, it boiled chiefly between 260–270° and especially at 267–268°. The fraction collected at 267–268° during the distillation has the density $d_{22.8}^{22.8} = 0.9204$ and the refractive index $n_D^{18} = 1.5040$.

0.1522 g. gave 0.4897 CO₂ and 0.1614 H₂O. C = 87.74; H = 11.79. C₁₅H₂₄ requires C = 88.16; H = 11.84.

It was a colorless, somewhat viscous liquid and had a characteristic odor. When a few drops of this fraction were dissolved in a few cc. of glacial acetic acid and shaken with one drop of concentrated sulfuric acid, the liquid assumed a feeble reddish color which turned to red with violet shade and on standing overnight it finally developed a brownish red color.

Preparation of Hydrochloride.—A hydrochloride was prepared by passing dry hydrogen chloride in a well-cooled solution of the substance in twice its volume of ether. The gas was readily absorbed and the liquid became brown. After saturation, it was kept four hours and on evaporating the ether crystals separated, which, after washing with glacial acetic acid, were recrystallized from acetic ether. The crystals, thus obtained, formed white needles, having a radial aggregation and melting at 117–118°.

0.2903 g. gave 0.2986 AgCl. Cl = 25.45%. C₁₅H₂₄·2HCl requires Cl = 25.59%.

Preparation of Hydrobromide.—The fraction was dissolved in twice its volume of glacial acetic acid and well cooled. A cold, saturated hydrogen bromide solution in glacial acetic acid was added in it and well shaken, when a crop of white, needle-like crystals separated which were washed with glacial acetic acid, drained on a porous tile, and finally

recrystallized from acetic ether. It melted at 124–125°. Thus the identification of this fraction with cadinene was confirmed.

From the results of this investigation, the following conclusion may be drawn:

The Formosan Hinoki wood oil consists chiefly of *d*- α -pinene and cadinene, with a small amount of oxygenated compounds. The amount of terpenes is about 70% and that of sesquiterpenes is about 24%.

Pinene hydrochloride may advantageously be purified by sublimation and it melts sharply at 132.5–133.5° (corr.).

TOKYO, JAPAN.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF VANDERBILT UNIVERSITY.]

ORGANIC MOLECULAR COMPOUNDS.

BY JAMES F. NORRIS.

Received December 23, 1915.

In a paper published sometime ago by Norris, Thomas, and Brown¹ it was shown that tetraphenylethylene dichloride, $(C_6H_5)_2CCl.ClC(C_6H_5)_2$, formed well-characterized molecular addition products with chloroform and with carbon tetrachloride. Since organic molecular compounds have been little investigated, it seemed advisable to study such compounds more fully in order to determine, if possible, the conditions necessary for their formation. It is evident that a satisfactory theory of valency must be susceptible of explaining the atomic relationships in molecular compounds; for these substances are as definite in their composition as the simpler compounds, which are explicable with our present inadequate views; and, moreover, certain so-called molecular compounds are known which are more stable than many possessing a simple atomic structure. Our present theories of valency, as applied to organic chemistry, do not cover the case of molecular compounds, and we cannot, therefore, predict what atomic conditions are necessary for the formation of a compound as the result of the union of two molecules. The field of organic chemistry is the best available for the investigation of these atomic conditions, since slight and graded changes in the combining power which holds the atoms together can be made by introducing into the molecule one or more groups the nature of which can be changed at will.

The results described below were obtained in a preliminary study of this problem. Work is actively in progress to determine, if possible, the causes that affect the mutual affinity between atoms in organic molecules, and the relationship between these affinities and the phenomenon of the formation of molecular compounds.

As has been emphasized of late, the bonds which unite atoms in an organic compound are markedly affected by the nature of the surround-

¹ Ber., 43, 2940 (1910).

ing atoms. For example, the union between the carbon atom and the chlorine atom in methyl chloride is quite different from that between the same elements in triphenylmethyl chloride. At present we have no absolute method of measuring this difference, and no way of representing it in our graphic formulas; but it is possible to get a definite conception of the relative activity of the corresponding atoms in a series of compounds of the same type. The results reported below have to do with the study of this problem from the standpoint of the formation of molecular compounds. It is not certain whether such substances are formed as the result of the existence of what might be called a molecular valency possessed by the two constituents of the compound, or whether the union is the result of the affinity residing on single atoms in each of the molecules. If the latter view be true, the atoms which are instrumental in forming the molecular compound possess in the simpler molecules a power of combination which comes into play when the union takes place. According to the accepted views, chloroform and carbon tetrachloride are saturated compounds, yet they are able to unite with other compounds. They possess, therefore, a power of combination which must be taken into account in an adequate theory of valency.

In order to guide the work undertaken to throw light on this question, a hypothesis was formulated and the deductions from it were tested. With our present conception of valency it seemed that more definite views susceptible of being tested could be arrived at by attributing the power of molecules to form compounds among themselves, to single atoms in these molecules. A working hypothesis was arrived at as the result of the following considerations: Every element contains a definite amount of chemical energy which undergoes transformation, in part, when it enters into combination with another element. The amount of chemical energy in the resulting compound is determined by the amount of energy transformed in its formation. This residual energy, which still is present in the atoms, makes it possible for the molecule to unite either with additional atoms, or with molecules to form molecular compounds. If, in the formation of the original molecule, a large share of the chemical energy is transformed, the resulting compound would have little power of union with other things; if, on the other hand, a small amount only of the chemical energy has been lost, the compound would exhibit in a marked degree the power to unite with other substances. If this residual energy is sufficient in amount, a compound with another element is possible, whereas if the amount is small a molecular compound may be formed. In general, the change in energy which takes place in the formation of molecular compounds is less than that transformed in the formation of simple compounds. For example, when phosphorus unites with chlorine to form phosphorus trichloride but a part of the available chemical energy

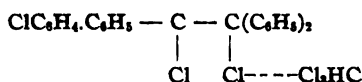
is transformed into heat. When the trichloride unites with chlorine to form the pentachloride more of the energy is transformed, but the latter compound still possesses available chemical energy. It is not sufficient in amount to react with more chlorine, but it can become available when the molecule is brought into contact with other molecules; many molecular compounds containing phosphorus pentachloride are known. When we write the formula of the compound as PCl_5 and consider the molecule a saturated one, the conclusion is not in accord with the facts. When one phosphorus atom unites with five chlorine atoms but a part of the available energy of the chlorine atoms is transformed; they, therefore, possess energy which can come into play in the formation of molecular compounds. Many compounds which contain a number of chlorine atoms, such as SbCl_5 , AsCl_5 , and SnCl_4 , form well-characterized molecular compounds with both inorganic and organic molecules. The above views are but a restatement of the electrochemical theory of Berzelius. It has often happened in the development of science that advance has come as a result of the application of the older theories to the facts which have been discovered since the enunciation of these theories. According to this view all compounds are probably unsaturated.

The application of this hypothesis in the case of tetraphenylethylene is as follows: The hydrocarbon, which has the formula $(\text{C}_6\text{H}_5)_2\text{C} = \text{C}(\text{C}_6\text{H}_5)_2$, exhibits an anomalous behavior; it will not form a dibromide when treated with bromine, and does not show the characteristic properties of an unsaturated compound. It is evident that the chemical affinity of the four phenyl groups almost completely "neutralizes" that possessed by the two carbon atoms. They do not contain enough available energy to permit of their union with bromine. It was shown that the hydrocarbon will unite with chlorine, however. In the resulting compound, tetraphenylethylene dichloride, the two chlorine atoms are very labile; they are removed easily by metals, and interact at room temperature with water. The two carbon atoms to which the chlorine atoms are attached do not hold the latter firmly, since they possessed but a small amount of available chemical energy which was transformed in the formation of tetraphenylethylene dichloride. As a result, according to the hypothesis put forward here, but a small amount of the chemical energy of the added chlorine has been expended in the union, and, as a consequence, a large share of it is left which can become available in the formation of molecular compounds. It is highly probable that if we could measure the heat of formation of tetraphenylethylene dichloride from the hydrocarbon and chlorine, we should find it much smaller in amount than the corresponding heat of formation of ethylene chloride. In the paper cited it was shown that tetraphenylethylene dichloride formed molecular compounds with chloroform and with carbon tetrachloride;

in this paper analogous addition products with bromoform, dichlorobromomethane, carbon tetrabromide, and sulfuryl chloride are described.

From the point of view which has been stated, it seemed probable that compounds which contained an active chlorine atom would possess the power to form molecular compounds. The activity of the chlorine atom in triphenylchloromethane, $(C_6H_5)_3CCl$, resembles that of the halogen atoms in tetraphenylethylene dichloride. Its activity can be traced to the same cause, namely, the fact that in establishing the union between the methane carbon atom and the halogen, but a small amount of chemical energy is transformed, and as a result, the chlorine atom in the chloride possesses a large share of its energy and is consequently active. In testing this view it was found that triphenylchloromethane forms molecular compounds with carbon tetrachloride and with acetone; other addition products are now being investigated. It is interesting to note in this connection that benzoyl chloride and analogous compounds which contain an active chlorine atom form molecular compounds; these, also, are now under investigation.

It has been shown by previous investigators that the ability to add bromine at the double bond in compounds of the type $R_2C = CR_2$ is markedly affected by the nature of the radicals joined to the ethylene carbon atoms. We have found that a number of compounds of this type which do not add bromine, form dichlorides. The ability of the latter to form molecular addition products is being studied. It has been found that *p*-chlorotetraphenylethylene unites with chlorine, and that the resulting dichloride forms molecular compounds with chloroform and carbon tetrachloride. The stability of these compounds is much less than that of the analogous addition products containing tetraphenylethylene dichloride. As was expected the compound containing carbon tetrachloride was the more stable; it contained two molecules of carbon tetrachloride. The chloroform addition product contained but one molecule of the added halogen compound. The introduction of chlorine into one of the benzene rings reduced the power of the resulting molecule to form addition products and made it unsymmetrical. The two ethylene carbon atoms do not possess the same degree of unsaturation, and, as a consequence, the chlorine atoms added to these might be expected to show different properties. It is highly probable that the formula for the chloroform addition product should be written thus:



to emphasize the fact that the halogen in one of the rings has weakened the power of one of the chlorine atoms to form molecular compounds. A study of tetrabromotetraphenylethylene dichloride brought out the

interesting fact, which might have been foretold from the facts just stated, that the compound did not possess the power to form molecular compounds with any of the substances investigated.

From the results obtained and the hypothesis put forward, we were led to investigate the possibility of the formation of molecular addition products by compounds other than those containing halogen atoms. From the point of view put forward it appeared probable that substances of two distinct classes might possess the power to form molecular compounds. The first class consists of compounds which possess an active element or group. The fact that such an element or group can be readily removed by reagents indicates that one factor in its activity is that it is not firmly bound in the compound, or, in other words, it contains a large amount of available energy. A study of compounds of this type is now being made. It has been found, for example, that triphenylcarbinol, which contains an active hydroxyl group, forms molecular compounds with acetone and with carbon tetrachloride. It is of interest to point out in this connection that the methane hydrogen atom in triphenylmethane can be readily replaced by other atoms or groups; it is unusually active for a hydrogen atom joined to carbon. Triphenylmethane forms a well-characterized molecular compound with benzene, and it was shown by one of us¹ that it forms a compound with aluminium chloride. It is highly probable that the hydrogen atom joined to the methane carbon atom furnishes the chemical energy which is involved in the formation of such molecular compounds. The hydrocarbon is being further investigated from this point of view.

The second class of substances which might possess the power to form molecular compounds are those containing so-called unsaturated carbon atoms which have largely lost their power to add other atoms as the result of the accumulation of negative groups around the unsaturated atoms. As has been pointed out the unsaturation of tetraphenylethylene and similar compounds is very slight. The available energy is not great enough in amount in most cases to bring about the reactions characteristic of highly unsaturated compounds like ethylene. The unsaturation may be great enough, however, to lead to the formation of molecular compounds. In confirmation of this view it was found that tetrabromotetraphenylethylene, which contains an inactive double bond, forms molecular compounds with acetone, methylethyl ketone, diethyl ketone, ethyl acetate, carbon tetrachloride, and benzene. Other compounds of this type are being studied. It is of interest to note in this connection that benzene forms a number of molecular compounds. The power to form such compounds is due, according to the views put forward here, to the fact that the unsaturation of benzene is very slight; it resembles that of the double bond

¹ *Am. Chem. J.*, 26, 499 (1901).

in tetraphenylethylene. The available energy is not sufficient in amount to permit the compound to add atoms readily, but is sufficient for the formation of molecular compounds, since in such formation small amounts of energy, are, in general, transformed.

The views put forward have led to the conclusion that the number of atoms with which any atom unites is not limited to the valence of the latter. The tendency of atoms to lose their chemical energy is the factor which leads to the formation of compounds. This loss can be brought about in steps. The number of possible steps when atoms or radicals are added is the valence of the element. When, however, a smaller expenditure of energy takes place, as in the addition of molecules, the number of steps can be increased. It is highly probable that the forces which bind together molecules are of the same nature as that which comes into play in the formation of simple compounds; the difference is one not of kind but amount.

The existence of many of the organic molecular compounds described in the literature can be explained from the point of view put forward here. A large amount of additional work must be done, however, to test the hypothesis stated. This will include a study of the effect of the nature of the radicals present in a compound on its ability to form molecular addition products. Since decrease in temperature is often associated with increase in combining power, it is probable that, at temperatures lower than that of the atmosphere, such an increase may lead to the formation of molecular compounds by substances which do not ordinarily exhibit this power. A study of the effect of temperature on the formation of molecular compounds is accordingly being made.

Experimental Part.¹

With KATHARINE E. ROONEY, JANET S. MURPHY and CAROLYN F. DODGE.

Preparation of Tetraphenylethylene Dichloride.—The tetraphenylethylene used throughout the work was prepared easily and in large quantities from benzophenone chloride and diphenylmethane according to the directions given in the paper referred to in the introduction. Directions for a convenient method of preparation of benzophenone chloride from carbon tetrachloride and benzene are also given in the same paper. In order to make tetraphenylethylene dichloride the hydrocarbon was dissolved in the smallest amount of chloroform and the solution was then saturated with dry chlorine. The solvent was next distilled off on a water bath, and the resulting crystals were recrystallized from a mixture of equal volumes of dry ethyl acetate and carbon bisulfide. The yield of the pure compound was about 90% of the theoretical. The compound forms large transparent crystals that melt at 160–162° with decomposition.

¹ The work described in the paper was done in the laboratory of Simmons College.

Preparation of the Compound $(C_6H_5)_2CCl.ClC(C_6H_5)_2.2CHBr_2$.—A compound of tetraphenylethylene dichloride and chloroform was described in the paper referred to in the introduction. Experiments with bromoform led to the preparation of an analogous compound. This addition product was prepared by saturating hot bromoform with tetraphenylethylene dichloride, and allowing the solution to cool. The crystals were filtered off and after drying in the air were analyzed by determining the loss in weight (bromoform) when heated in a Victor Meyer bath containing boiling water, the temperature of the inside of the bath being 92° .

1.6235 g. came to const. wt. in 3 hrs. and lost 0.9052 g. Calcd. loss in wt. for the formula given above, 55.67%. Found, 55.75%.

The composition of the addition product was also determined by synthesis. A weighed quantity of tetraphenylethylene dichloride was placed in a desiccator with a vessel containing bromoform, and kept until the dichloride came to a constant weight. On account of the slight volatility of bromoform the addition took place very slowly; the weight was constant at the end of ten weeks. The tetraphenylethylene dichloride used was obtained by allowing the crystals of its addition product with chloroform to lose the latter at room temperature; it was in the form of a friable porous mass.

1.0733 g. of tetraphenylethylene dichloride increased in wt. 1.3467 g. Calcd. for $(C_6H_5)_2CCl.ClC(C_6H_5)_2.2CHBr_2$: 125.6%. Found: 125.4%.

Preparation of the Compound $(C_6H_5)_2CCl.ClC(C_6H_5)_2.2CBr_4$.—A compound of tetraphenylethylene dichloride and carbon tetrachloride was described in the paper cited above. The addition product with carbon tetrabromide was prepared by dissolving the compound and tetraphenylethylene dichloride in carbon disulfide and allowing the solution to evaporate spontaneously. Solutions were prepared containing the constituents in the molecular ratio of one of the dichloride to one of carbon tetrabromide and of one of the former to two of the latter. The same compound was obtained in the two cases. It melted at $144-147^\circ$. The substance was analyzed by heating it to constant weight at 92° in a Victor Meyer bath.

1.3220 g. lost 0.8394 g. in 36 hrs. when heated to const. wt. Calcd. for $(C_6H_5)_2CCl.ClC(C_6H_5)_2.2CBr_4$: 62.23%. Found: 63.42%.

Preparation of the Compound $(C_6H_5)_2CCl.ClC(C_6H_5)_2.2CHBrCl_2$.—The compound was prepared by crystallizing the dichloride from hot dichlorobromomethane. It resembled in appearance the analogous chloroform compound.

0.8677 g. lost 0.4165 g. in 1 hr. at 92° . Calcd. for $(C_6H_5)_2CCl.ClC(C_6H_5)_2.2CHCl_2Br$: 44.87%. Found: 47.99%.

Preparation of the Compound $(C_6H_5)_2CCl.ClC(C_6H_5)_2.2SO_2Cl_2$.—This compound was prepared by crystallizing tetraphenylethylene dichloride

from hot sulfuryl chloride. It was also formed by placing a sample of tetraphenylethylene chloride in a desiccator containing sulfuryl chloride. The compound crystallizes in shiny, transparent crystals, which effloresce rapidly and are readily decomposed by the moisture of the air. Analysis indicated that the formula was that given above although concordant results were not obtained on account of the instability of the compound.

Preparation of the Compound $p\text{-ClC}_6\text{H}_4\text{.C}_6\text{H}_5\text{.CCl.ClC(C}_6\text{H}_5)_2\text{.CHCl}_3$.—*p*-Chlorotetraphenylethylene was prepared as described in the article cited above. It was purified by the method described below. The compound was formed by boiling together as long as hydrogen chloride was evolved a mixture of *p*-chlorobenzophenone chloride and diphenylmethane. The product was distilled and the part which solidified was crystallized repeatedly from hot alcohol, and finally from glacial acetic acid, when it was obtained in small crystals which melted at $165\text{--}167^\circ$. The compound was dissolved in chloroform and the solution saturated with dry chlorine. On evaporation a gummy mass was obtained. When this was dissolved in acetone and the solution was allowed to evaporate, well-formed crystals of *p*-chlorotetraphenylethylene dichloride were obtained. The compound is readily soluble in chloroform, carbon tetrachloride, and petroleum ether; it dissolves with difficulty in cold acetone, and readily in hot acetone. It melts at $135\text{--}137^\circ$.

The addition product of *p*-chlorotetraphenylethylene dichloride and chloroform was prepared by saturating warm chloroform with the dichloride and cooling the resulting solution in a mixture of ice and concentrated hydrochloric acid. The product was obtained in shiny, cubical crystals resembling the analogous compound containing tetraphenylethylene. It melted at $58\text{--}59^\circ$. It loses chloroform rapidly in the air.

0.4643 g. lost 0.0869 g. at 92° . Calc. for $\text{ClC}_6\text{H}_4\text{.C}_6\text{H}_5\text{.CCl.ClC(C}_6\text{H}_5)_2\text{.CHCl}_3$: 21.42%. Found: 18.72%.

Preparation of the Compound $\text{ClC}_6\text{H}_4\text{.C}_6\text{H}_5\text{.CCl.Cl(C}_6\text{H}_5)_2\text{.2CCl}_4$.—The compound was prepared by crystallizing the dichloride from carbon tetrachloride. The crystals which separated on cooling melted at $91\text{--}93^\circ$. As the carbon tetrachloride was lost quickly in the air it was difficult to obtain a sample for analysis free from mechanically held solvent and at the same time prevent loss of the chemically combined carbon tetrachloride. The stability of this compound is markedly different from the one of analogous composition containing tetraphenylethylene dichloride.

0.5664 g. lost 0.257 g. at 92° . Calc. for $\text{ClC}_6\text{H}_4\text{.C}_6\text{H}_5\text{.CCl.ClC(C}_6\text{H}_5)_2\text{.2CCl}_4$: 42.7%. Found: 46.3%.

Preparation of the Compound $p\text{-(BrC}_6\text{H}_4)_2\text{C}=\text{C(C}_6\text{H}_4\text{Br)}_2$.—An improved method of preparing this compound is as follows: To 5 g. of tetraphenylethylene, which has been ground to a fine powder and is spread out in a thin layer, are added 7.5 cc. of bromine in small portions

and with stirring. When the excess of bromine has evaporated, the product is crystallized from boiling acetone, in which it is not very soluble. It is obtained in shiny crystals which contain acetone (see below). When heated the acetone is lost and the compound then melts at $251-252^{\circ}$. The yield of the pure compound is about 65% of the theoretical.

Preparation of the Compound $(\text{BrC}_6\text{H}_4)_2\text{CCl.ClC}(\text{C}_6\text{H}_4\text{Br})_2$.—The compound was prepared by saturating a solution of tetrabromotetraphenylethylene in carbon tetrachloride with dry chlorine. The solution is next evaporated to dryness and the residue crystallized from a hot mixture of equal volumes of carbon disulfide and ethyl acetate. The compound melts at $190-192^{\circ}$. Unsuccessful attempts were made to prepare addition products of the compound with chloroform and carbon tetrachloride.

Preparation of the Compound $(\text{BrC}_6\text{H}_4)_2\text{C} = \text{C}(\text{C}_6\text{H}_4\text{Br})_2.2(\text{CH}_3)_2\text{CO}$.—Tetrabromotetraphenylethylene crystallizes from acetone in shiny needles which become opaque when allowed to stay in the air.

0.9642 g. of substance lost 0.1357 g. at 92° . Calc. for the formula given above: 15.09%. Found: 14.06%. Another sample which was allowed to stand 4 minutes in the air after all visible acetone had been removed lost 15.53% when heated to constant weight.

Preparation of the Compound $(\text{BrC}_6\text{H}_4)_2\text{C} = \text{C}(\text{C}_6\text{H}_4\text{Br})_2.\text{CH}_3\text{COC}_2\text{H}_5$.—This compound was prepared by crystallizing the substituted hydrocarbon from methylethyl ketone. The molecular compound is much more stable than the acetone addition product.

0.7410 g. substance lost 0.0727 g. at 92° . Calc. for the formula given above: 10.00%. Found: 9.81%.

Preparation of the Compound $(\text{BrC}_6\text{H}_4)_2\text{C} = \text{C}(\text{C}_6\text{H}_4\text{Br})_2.(\text{C}_2\text{H}_5)_2\text{CO}$.—The addition product was prepared by crystallizing the substituted hydrocarbon for diethyl ketone. It crystallizes in long, lustrous needles.

0.6806 g. of substance lost 0.0842 g. at 92° . Calc. for the above formula: 11.71%. Found: 12.37%.

Preparation of the Compound $(\text{BrC}_6\text{H}_4)_2\text{C} = \text{C}(\text{C}_6\text{H}_4\text{Br})_2.\text{CCl}_4$.—This compound was formed when tetrabromotetraphenylethylene was crystallized from carbon tetrachloride. The compound forms small crystals which effloresce rapidly.

0.4421 g. lost 0.0803 g. Calc. for the above formula: 19.20%. Found: 18.17%.

Preparation of the Compound $(\text{BrC}_6\text{H}_4)_2\text{C} = \text{C}(\text{C}_6\text{H}_4\text{Br})_2.\text{CH}_3\text{COOC}_2\text{H}_5$.—This compound, prepared by crystallization from ethyl acetate, was relatively stable. When a gram was exposed to the air at room temperature it lost ethyl acetate at the rate of one milligram in 10 minutes.

0.9032 g. lost 0.1105 g. at 92° . Calc. for the above formula: 11.96%. Found: 12.17%.

Preparation of the Compound $(\text{BrC}_6\text{H}_4)_2\text{C} = \text{C}(\text{C}_6\text{H}_4\text{Br})_2.\text{C}_6\text{H}_6$.—The compound formed large, lustrous needles.

1.3694 g. lost 0.1549 g. at 92°. Calc. for the above formula: 10.75%. Found: 11.32%.

Preparation of the Compound $[(C_6H_5)_3COH]_3[CCl_4]_3$.—Triphenylcarbinol crystallizes from hot carbon tetrachloride on cooling in large, flat, square crystals. They begin to effloresce on being exposed to the air and soon become opaque. The compound was repeatedly prepared and analyzed on account of the fact that the analytical results did not agree with the simple formula that was anticipated from a consideration of the composition of the analogous compounds. The time during which the crystals were allowed to stand in the air was varied. The losses in weight in a series of analyses were as follows: 30.44, 30.87, 31.06 and 30.77%. The calculated loss for a compound containing one molecule of each constituent is 37.19% and for one containing two of the carbinol to one of carbon tetrachloride is 22.84%. The calculated loss for a compound of the formula given above is 30.75%.

Preparation of the Compound $[(C_6H_5)_3COH]_2(CH_3)_2CO$.—Triphenylcarbinol crystallizes from acetone in large, transparent, prismatic crystals which effloresce slowly.

0.6022 g. lost 0.0613 g. when heated to constant weight. Calc. for a compound of the above composition: 10.06%. Found: 10.18%.

Preparation of the Compound $(C_6H_5)_3CCl.CCl_4$.—Triphenylchloromethane crystallizes from carbon tetrachloride in small, lustrous crystals which do not effloresce rapidly in the air.

0.5073 g. lost 0.1444 g. at 92°. Calc. for the above formula: 28.92%. Found: 28.46%.

Preparation of the Compound $[(C_6H_5)_3CCl]_2(CH_3)_2CO$.—A compound of this composition was obtained by allowing a solution of triphenylchloromethane in acetone to evaporate spontaneously. The addition product is relatively stable.

0.5916 g. lost 0.0553 g. at 92°. Calc. for the above formula: 9.43%. Found: 9.35%.
NASHVILLE, TENNESSEE.

[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE, UNIVERSITY OF PITTSBURGH.]

ON THE DETECTION AND DETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS.

BY I. DROGIN AND M. A. ROSANOFF.

Received January 13, 1916.

Some years ago C. W. Bacon,¹ at the instance of one of us (M. A. R.), undertook to test an apparently valuable method for determining halogens in organic compounds that had been recommended by Stepanoff in 1906.²

¹ Bacon, *THIS JOURNAL*, 31, 49 (1909).

² Stepanoff, *Ber.*, 39, 4056 (1906).

Stepanoff's method consisted in dissolving the given halogen compound in 98% alcohol and adding a certain excess of metallic sodium; later, diluting with water, distilling off the alcohol, acidifying with nitric acid and, finally, measuring the freed halogen acid by Volhard's method. Bacon followed Stepanoff's directions scrupulously, yet the results were unsatisfactory. Then, in view of the great simplicity of Stepanoff's method and its obvious advantages over the generally used method of Carius, Bacon undertook to improve Stepanoff's directions, and after a certain amount of experimenting believed to have succeeded in developing Stepanoff's principle into a universally reliable analytical method. In his paper, Bacon reports a series of successful analyses of some decidedly refractory compounds, including ten consecutive analyses of hexachlorobenzene. The problem thus appeared to be solved.

Two years later Stepanoff's method was independently investigated by C. H. Maryott.¹ At the suggestion of Professor Van Name, Maryott substituted potassium in place of the sodium used by Stepanoff, and analyzed chlorobenzene, bromobenzene, hexachlorobenzene, and *p*-chloroaniline, with sufficiently good results. Maryott claims greater rapidity for his method by comparison with the sodium method as recommended by Bacon.

Bacon's directions, on the other hand, were investigated by Walker and McRae,² but with unsatisfactory results:-

"With Bacon's method," they say, "about forty trials were made [in the case of bromobenzene], all of the results being low, and in no case were duplicates obtained which agreed, which showed that the reduction was incomplete and irregular." Walker and McRae were "forced to conclude, therefore, that this method is not of general applicability, and especially cannot be used with difficultly reducible substances."

Most of the results obtained by Walker and McRae were only one or two per cent. low. Bacon himself, as already stated, had obtained a series of very good results indeed. It appeared possible, therefore, that Stepanoff's principle might yet be developed into a desirable analytical method by an appropriate modification of Bacon's procedure. And when, early in 1915, another investigation in which the present authors were engaged had to be temporarily interrupted, it was decided to re-investigate the halogen problem and make a new attempt to render fruitful the principle employed by Stepanoff.

A series of trials according to the directions recommended by Bacon soon convinced us that Walker and McRae were right, and that those directions were really somewhat imperfect. Another series of trials, in which we followed the directions given by Maryott, using *m*-bromobenzoic acid, yielded still poorer results, and even when the amount of potassium used was four or five times that specified by Maryott, our

¹ Maryott, *Am. J. Sci.*, **30**, 378 (1910); *Chem. News*, **103**, 1 (1911).

² *THIS JOURNAL*, **33**, 598 (1911).

figures were still several per cent. below the theoretical percentage. Possibly Maryott may have neglected to mention some essential detail of manipulation.

We then undertook a systematic series of experiments, gradually modifying Bacon's method in its several steps; and at last our efforts were, we think, successful. We found that increasing Bacon's amount of sodium by 10% and, at a later stage, carrying out the Volhard halogen determination with all necessary care, led to *uniformly excellent results in all cases without exception*. This, we believe, is fully enough demonstrated below by the results of *sixty-four consecutive analyses* of eleven substances belonging to different classes. In order to positively insure success in the use of the method by others, the directions will be stated in great detail.

Directions.

The required reagents are: (1) absolute alcohol; (2) metallic sodium; (3) pure nitric acid; (4) a *N/15* solution of silver nitrate; (5) a *N/15* solution of ammonium thiocyanate; and (6) a solution of ferric ammonium alum.

Remarks Concerning the Reagents.—Ordinary absolute *alcohol* should be redistilled from metallic sodium, about 10 g. of sodium being used per liter of alcohol. As a precaution against any possible oxidation of the alcohol, the distillation may be carried out in a slow stream of dry hydrogen. The sodium should be carefully tested for the presence of halogens. The best commercial sodium will be found to be sufficiently pure. If only a less pure metal is available, a determination of its chlorine content must be carried out on a sample of at least 10 g., and subsequently the error due to this source corrected.¹ The oxide film on the surface of the metal should be removed, and the bright pieces weighed and kept for use under kerosene oil. The *nitric acid* and the water used should, of course, be halogen free; the reagent should contain one part of the concentrated acid to three parts of water. The *N/15* solution of *silver nitrate* may be made up by dissolving 11.326 g. of the dry salt in water and diluting to one liter. Naturally, the exact strength of the solution must be determined either gravimetrically, or volumetrically by titration against a hydrochloric acid of precisely known strength.² The *ammonium thiocyanate* reagent may be made up by dissolving 5.075 g. of the pure dry salt in water and diluting to one liter. The exact strength of the solution is determined by titration against the above silver nitrate solution. The *ferric salt indicator* is made up by preparing a solution of ferric ammonium alum as nearly saturated as possible, and adding concentrated nitric acid until the original red of the solution has turned to straw-yellow.

¹ The sample of sodium used by ourselves required a correction of from 0.1 to 0.2 in the percentage of halogen in the compounds.

² See Hulett and Bonner, *THIS JOURNAL*, 31, 390 (1909).

Amounts of Alcohol and Sodium Required.—A large number of experiments have demonstrated that the following relative quantities of alcohol and sodium are necessary and sufficient for the complete extraction of the halogens from apparently any organic combination. If W denotes the weight of substance taken (between 0.2 and 0.3 g.), and if the halogen in the given compound is *chlorine*, then the number of cubic centimeters of alcohol in which the substance is to be dissolved, should be $156W$; the number of grams of sodium to be used then is $21.5W$. If the given compound contains bromine, then $68W$ cc. of alcohol and $9.4W$ g. of sodium should be used. If the compound contains *iodine*, then $44W$ cc. of alcohol and $6.1W$ g. of sodium should be used.

Principal Operation.—From 0.2 to 0.3 g. of the substance to be analyzed is introduced into a dry Kjeldahl flask of 300 cc. capacity, the required amount of absolute alcohol is added, and the flask attached to a Liebig reflux condenser (the constricted end of the inner tube of the condenser is best cut off). The contents of the flask are now warmed with a burner flame placed under an asbestos gauze; when the solid has dissolved, the flame is turned out, and the gradual introduction of the sodium is begun. Small pieces of the metal are removed from the kerosene in which they have been kept, rapidly dried with filter paper, and rolled out into little rods, which are dropped into the solution through the condenser. At no time should there be more than, say, three pieces of undissolved sodium together in the flask. *The introduction of the sodium should take altogether about thirty minutes*, and during at least the second half of the time the dissolution of the sodium should be aided by a small flame under the flask. After all the sodium has been introduced the solution should be allowed to boil gently *for a full hour*, during which it should be shaken three or four times to help dissolve the metal. Sometimes even this does not suffice to dissolve the last particles of metal; but a small undissolved remnant is harmless. Now, after cooling, the contents of the flask are diluted through the condenser with water, 1 cc. at a time being added at first, as long as vigorous action ensues. The total volume of the diluted solution should be about 250 cc. Carbonization, which at times occurs during dilution, is harmless. Next the solution, while kept cool with tap-water, is acidified with the 1 to 3 nitric acid reagent (the addition of nitric acid generally causes considerable reduction of the reddish color of the diluted alkaline solution).¹

On transferring the acidified contents of the Kjeldahl flask into a large beaker, a measured amount of silver nitrate solution is added, sufficient to precipitate the entire halogen present and about 3–4 cc. in excess. The

¹ If the halogen involved is iodine, the alkaline solution should be acidified more slowly and with much greater caution; it should be thoroughly cooled with ice, and a much more dilute nitric acid employed.

precipitate is filtered off,¹ the filtrate being allowed to run into a *porcelain dish of about one liter capacity*. To the filtrate are added 10 cc. (no less) of the ferric indicator, and then ammonium thiocyanate is run in, to the ap-

RESULTS.

I. Chlorobenzene, C_6H_5Cl .		II. Bromobenzene, C_6H_5Br .		III. Hexachlorobenzene, C_6Cl_6 .	
Theory, 31.52% chlorine.		Theory, 50.92% bromine.		Theory, 74.71% chlorine.	
Chlorine found. Per cent.	Difference. Per cent.	Bromine found. Per cent.	Difference. Per cent.	Chlorine found. Per cent.	Difference. Per cent.
31.34	-0.18	50.78	-0.14	74.59	-0.12
31.33	-0.17	50.79	-0.13	74.61	-0.10
31.51	-0.01	50.75	-0.17	74.61	-0.10
31.38	-0.14	50.82	-0.10	74.60	-0.11
31.31	-0.21	50.86	-0.06	74.59	-0.12
		50.84	-0.08	74.61	-0.10
IV. Benzene Hexachloride, $C_6H_2Cl_4$.		V. <i>m</i> -Chlorobenzoic Acid, $C_6H_4ClCO_2H$.		VI. <i>p</i> -Chlorobenzoic Acid, $C_6H_4ClCO_2H$.	
Theory, 73.16% chlorine.		Theory, 22.66% chlorine.		Theory, 22.66% chlorine.	
Chlorine found. Per cent.	Difference. Per cent.	Chlorine found. Per cent.	Difference. Per cent.	Chlorine found. Per cent.	Difference. Per cent.
73.22	+0.06	22.66	0.00	22.60	-0.06
73.21	+0.05	22.63	-0.03	22.60	-0.06
73.26	+0.10	22.54	-0.12	22.67	+0.01
73.08	-0.08	22.58	-0.08	22.54	-0.12
73.23	+0.07	22.61	-0.05	22.62	-0.04
		22.60	-0.06	22.63	-0.03
VII. <i>m</i> -Bromobenzoic Acid, $C_6H_4BrCO_2H$.		VIII. <i>p</i> -Bromobenzoic Acid, $C_6H_4BrCO_2H$.		IX. Benzyl Chloride, $C_6H_5CH_2Cl$.	
Theory, 39.77% bromine.		Theory, 39.77% bromine.		Theory, 28.03% chlorine.	
Bromine found. Per cent.	Difference. Per cent.	Bromine found. Per cent.	Difference. Per cent.	Chlorine found. Per cent.	Difference. Per cent.
39.71	-0.06	39.67	-0.10	27.94	-0.09
39.71	-0.06	39.66	-0.11	27.81	-0.22
39.67	-0.10	39.71	-0.06	27.95	-0.08
39.75	-0.02	39.68	-0.09	28.10	+0.07
39.68	-0.09	39.64	-0.13	27.96	-0.07
39.64	-0.13	39.78	+0.01	27.96	-0.07
X. α -Bromonaphthalene, $C_{10}H_7Br$.		XI. Iodoform, CHI_3 .			
Theory, 38.61% bromine.		Theory, 96.70% iodine.			
Bromine found. Per cent.	Difference. Per cent.	Iodine found. Per cent.	Difference. Per cent.		
38.60	-0.01	96.39	-0.31		
38.60	-0.01	96.62	-0.08		
38.47	-0.14	96.49	-0.21		
38.51	-0.10	96.57	-0.13		
38.53	-0.08	96.44	-0.26		
38.65	+0.04	96.52	-0.18		

¹ See Rosanoff and Hill, THIS JOURNAL, 29, 269 (1907). In the analyses reported in the present paper the silver halide precipitates were invariably filtered off, bromide and iodide as well as chloride.

pearance of a faint but distinctly perceptible pink color. An additional two drops of the thiocyanate solution should make the color quite strong and prove that the true end point had been attained.

The Handling of Liquid Substances.—In analyzing liquids we used a glass tube 30 mm. long and 6 mm. in internal diameter, one end of the tube being sealed with a thickness of 3–4 mm. of paraffin wax. During the weighing, the tubelet was closed with a cork, which was removed immediately before tubelet and substance were introduced into the alcohol in the Kjeldahl flask.

A Qualitative Test for Halogen.

Our uniform success with the method described above suggested its use also as a qualitative test for halogens in organic compounds. A series of trials, using *p*-chlorobenzoic acid, *o*-chlorophenol, bromobenzene, bromonaphthalene, and iodoform, showed that the merest traces of halogen can be positively detected by the following simple procedure:

A few milligrams of the given substance are dissolved in one cubic centimeter of pure absolute alcohol; a few small bright pieces of pure metallic sodium are thrown into the solution, one at a time, with gentle warming toward the end; on cooling, the solution is acidified with 1 cc. of dilute nitric acid (3 parts of water to 1 part of acid), and filtered, if necessary; after testing the acidity of the solution, 10 drops of an approximately $N/15$ silver nitrate solution are added. A parallel blank test will of course make the result surer.

In this way, for instance, we plainly detected chlorine in 1 drop of a liquid produced by adding a single drop of carbon tetrachloride to 30 cc. of benzene. In the same case the Beilstein test gave a doubtful result.

PITTSBURG, PA.

A POSSIBLE SOURCE OF ERROR IN COLORIMETER OBSERVATIONS.

By J. H. LONG.

Received December 27, 1915.

Something over a year ago, in a series of observations just started, and in which a Duboscq colorimeter was employed, I noticed a marked variation from an anticipated result. The instrument had been in use for years and had always shown a correct zero point when the bottom of the glass cell and the plunger prism were brought in contact.

The standard colored liquid was in the left-hand cell and the one under investigation in the right. The observed column lengths were about 80 and 100. (The exact values are not recalled, but these are given to illustrate the situation.) The concentration of the investigated liquid was therefore about 80% of the other. On reversing the liquids, that is, putting the standard in the right-hand cell and adjusting the plunger to

80 divisions the reading on the left was found to be about 91 divisions. This made the apparent strength of the unknown about 88% of the standard strength.

This discrepancy suggested that the actual lengths of the liquid columns must be different from those read off, which would be the case if the plungers had dropped from their normal positions. A control of the zero point showed this to be the fact; one plunger had dropped about three millimeters, and the other five, or six and ten divisions, respectively. The column lengths first observed were then actually 74 and 90, giving 82, in place of 80% strength as the relation of the liquid to the standard.

After the reversal of the two liquids we have actually on the right side 70 divisions, against 85 on the left, as the real length of the liquid columns, which gives the correct relation. The sinking of the prism plungers had shortened the two columns in unequal degrees, giving rise to rather large errors. The prisms seem to be fastened in their brass sockets by means of a wax which is too soft for the purpose and which softens enough in our summer climate to allow the prisms to drop down a little. The situation described here was noticed after the instrument had stood through a hot summer vacation in a room facing the south and west, the temperature in which often reached 33°. Experiment showed that at this temperature the wax became appreciably softer, and soft enough to permit the slow displacement of the glass. I have since noticed the same defect in other instruments of the same type. Even greater errors are possible where the instrument is allowed to stand near a radiator or in a room where the temperature is always too high from overheating by steam. The prisms may even drop from their sockets in instruments left in this way.

If both prisms should drop to the same extent the error might be smaller but would not disappear. Assume, for example, that with the standard liquid in one cell the prism is set to give a depth of 10 millimeters in the column below. Or, in the form of instrument in which the cell and not the prism is moved, the former is brought up to make this apparent length of liquid column. In the other cell a depth of 12 millimeters is necessary to give the same shade. The concentrations of the liquids would then appear to be related as 12 to 10. If both prisms had dropped to the same degree, say 3 millimeters each, the actual lengths of the liquid columns would be, not 10 and 12, but 7 and 9. The relation of these lengths is no longer the same. Great errors are possible where short liquid columns are employed, and with unequal displacement of the prisms the weaker liquid may actually appear the stronger. For example, with an apparent depth of column in the standard cell of 10 millimeters, or divisions, the color equality in the other cell is reached with a depth of 8 millimeters, or divisions, of the scale. The strength of the unknown

liquid would then appear to be five-fourths of that of the standard. But if the prism in the standard cell had dropped 5 divisions, and the other only 2, for example, the actual lengths of columns of liquid would be 5 and 6 divisions, respectively, with the unknown having then a strength five-sixths of that of the other.

In the well-known creatinine estimation, where relatively long columns are employed, such large errors are not possible, but in many other comparisons, with short columns, they doubtless actually occur. It is therefore desirable to control the zero point frequently by bringing the end of the prism in contact with the bottom of the cell and noting that the reading is at the end or zero of the scale. Care should be taken to keep the instrument away from the vicinity of steam radiators, and, in general, in a place where the temperature does not become high in summer.

Others may have had similar experiences with the Duboscq instrument, but as I have not seen them discussed in print I think it worth while to call attention to the facts in this way.

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[CONTRIBUTION FROM THE LABORATORY OF THE KENTUCKY AGRICULTURAL EXPERIMENT STATION, LEXINGTON, KENTUCKY.]

CHEMICAL CHANGES OCCURRING DURING THE RIPENING OF THE WILD GOOSE PLUM.¹

By J. S. MCHARGUE.

Received January 17, 1916.

The beginning of the study of chemical changes that take place during the ripening of fruits dates back to the time of the phlogiston theory.

Sennebier,² after experimenting on a variety of fruits, supposed that they suffered a loss of phlogiston during the ripening process.

De Saussure,³ about 1820, carried on researches on the ripening of fruits and as a result of his investigations advanced the theory that fruits act like leaves in their respiratory functions. The fallacy of his theory was later shown by Berard,⁴ who carried on respiration experiments on fruits in vessels containing hydrogen, nitrogen, carbon dioxide, and *in vacuo*. In all cases he found an increase of carbon dioxide at the expense of the oxygen, and in no case the reverse change. Similar experiments were tried on fruits still attached to the tree, with the result that the fruit did not mature, but became withered and browned, showing that oxygen is necessary for the ripening of fruits. Apparently the work

¹ Read before the Lexington Section of the American Chemical Society, January 13, 1916.

² *J. pharm. chim.*, [2] 7, 249 (1821).

³ "Recherches Chimiques sur la vegetation," Paris, 1840.

⁴ *Ann. chim. phys.*, [2] 16, 152, 225 (1821).

of Berard affords us the first correct conception on the respiration of fruits.

The amount of acid in fruits and its supposed transformation during ripening has been the subject for much discussion and many theories. Among the earlier investigators it was assumed that the acid which was present in the unripe condition was transformed into sugar in the process of ripening.

In 1866 Pasteur¹ cast doubt on this theory by showing that in certain varieties of grapes the acid increased rather than diminished.

Kelley² also has recently shown that during the ripening of the pineapple the amount of acid increases.

In a review of the literature of more than sixty different authors on this subject, the two cases cited are the only ones in which an increase in the acidity during the ripening is recorded. All other investigations pertaining to acidity show a diminution.

However, a recent theory has been advanced which accounts for the diminution in the acidity during the ripening period by assuming that the acid undergoes decomposition, giving rise to carbon dioxide and water.

Famintzin,³ in 1871, published the results of his study on the ripening of grapes, which offers the first satisfactory explanation on the source of the sugars which appear in the grape on ripening. Chemical and microscopical methods were used. He states that the unripe grape contains no starch but that the stems of the grape are full of starch, which disappears as the grapes ripen.

Hilger⁴ confirmed the work of Famintzin and showed that the increase of sugar during a period of six days at the time of ripening was from 3.87 to 7.70% in one variety and from 5.33 to 7.71% in another, during which time the starch in the stems disappeared.

Considerable discussion has been evolved concerning what transformations tannin undergoes during the ripening process. Certain investigators have assumed that tannin is transformed into sugars; others claim that it undergoes complete decomposition and gives rise to carbon dioxide.

Lloyd,⁵ in a recent publication, states that the loss of astringency in persimmons during the process of ripening is due to the union of tannin with an associated colloid of a carbohydrate nature.

The occurrence of cane sugar in fruits has been noted in a number of instances; however, no particular significance has yet been attributed to its presence.

The above remarks review briefly some of the more important theories

¹ "Weinlaube," 1870, p. 274; also *Ann. Oenol.*, 2, 241 (1871).

² *J. Ind. Eng. Chem.*, 3, 403-405 (1911).

³ *Ann. Oenol.*, 2, 242 (1871).

⁴ *Landw. Vers.-Stat.*, 17, 245 (1874).

⁵ *Science (N. S.)*, 34, 924-928 (1911).

concerning the transformations and changes taking place during the maturation and ripening of fruits in general.

Rather late in the season of 1915 the writer's attention was called by the director of this Experiment Station to the changes taking place in the ripening of the wild goose plum, and a preliminary investigation was suggested, the object of which was to trace some of the changes taking place in the later stages of maturation.

The wild goose plum (*Hortulana*) is native to North America and apparently thrives best in the central and southwest portions of the United States. The term "wild goose" is of comparatively recent origin, and according to Hedrick¹ it received the name as follows:

About the year 1850, a farmer who lived in the vicinity of Columbia, Tennessee, fired into a flock of wild geese that was passing over his farm and succeeded in bringing down a goose. In dressing the fowl a plum seed was found in its craw, which was planted with some care. In the following spring a young plant came up from the seed, which in due course of time produced a tree and bore a fruit, which excelled in many respects any variety of plum that had ever been known to grow in that vicinity. Naturally the new fruit was called the wild goose plum.

This variety of plum is well adapted to the climatic conditions of Kentucky and because of its sweet taste and large size it has become a favorite with many fruit growers in this state.

The fruit reaches maturity in the latter part of July, and in its last stages of maturation passes rather rapidly through three stages of ripening, which are apparent to both the sense of sight and to taste.

As the fruit approaches maturity its color changes from a green to a slightly yellowish hue, and is more or less translucent in appearance. At this stage the fruit is sharply acid and somewhat astringent to the taste. In the course of from two to three days' time the fruit has changed from the yellowish hue to a bright pink color. The fruit at this stage is quite juicy and sweet to the taste, apparently all acidity and astringency having disappeared. It was also observed that at this stage many of the plums split or burst their skin. Usually the split was vertical rather than horizontal to the normal position of the plum. This bursting is quite pronounced in this variety of plum and has also been observed in other fruits and is in all probability due to internal pressure developed from chemical changes occurring during the ripening process.

After the plums have reached the pink or just-ripe stage, the color changes, after about 48 hours, to a dark red. The fruit at this stage has lost some of its juicy nature and the taste is decidedly less sweet.

Samples representing the fruit in the first and second stages of ripeness were collected from the tree and the sample for the third stage was ob-

¹ "The Plums of New York," p. 378.

tained by allowing some of the fruit gathered from the tree at the second stage of ripening to pass into the third, or overripe stage, under normal conditions. Determinations of acidity, reducing sugar and cane sugar were made on samples of the fruit at each of the three different stages of ripeness. Tests were also made at each of these stages for tannin. None was present as shown by the ferric chlorid test.

Table I shows the average of three determinations in each of the three different stages of ripening:

TABLE I.—SHOWING SOME OF THE CHEMICAL CHANGES OCCURRING IN THE RIPENING OF THE WILD GOOSE PLUM.

Different stages of ripening.	Acidity in terms of cc. 0.1 N NaOH per g. of plum.	Reducing sugar. In per cent.	Cane sugar. In per cent.	Total sugars. In per cent.
Unripe or beginning to turn yellow	3.08	5.82	0.40	6.22
	3.12	5.89	0.20	6.09
	3.19	6.04	0.65	6.69
Average.....	3.13	5.91	0.41	6.33
Ripe or sweet stage.....	2.62	6.90	3.60	10.50
	2.74	6.74	3.54	10.28
	2.72	6.93	3.70	10.63
Average.....	2.69	6.85	3.61	10.47
Overripe stage.....	2.33	9.17	0.61	9.78
	2.46	9.29	0.64	9.93
	2.40	9.02	0.46	9.48
Average.....	2.40	9.16	0.57	9.73

From the foregoing table it is apparent that some very marked and interesting changes take place in the acidity and in the amount of the reducing and cane sugars formed during the process of ripening of this plum. In the first place there is a decided loss in the acidity in passing from the first stage of ripening to the just-ripe stage. This loss is 14.05% of the acid found in the unripe stage. In passing from the ripe to the overripe condition there is a loss of 10.78%, which is 3.27% less than the loss in passing from the unripe to the ripe stage. The total loss in the acidity in passing from the unripe to the overripe stage was 23.32% of the acidity present in the unripe condition.

It is also interesting to note that as the acidity decreased there was a gradual increase in the amount of reducing sugar formed in each of the different stages of ripening. In passing from the unripe to the ripe stage there was an increase of 15.90% of reducing sugar formed, and in passing from the ripe to the overripe stage an increase of 33.72% and a total increase of 54.99% in passing from the unripe to the overripe stage.

The point of most interest in this investigation is the rapid formation

of cane sugar in passing from the unripe to the ripe condition and its subsequent inversion in passing from the ripe to the overripe condition. In the unripe stage we have less than 0.5% of cane sugar present, whereas in the ripe stage we have as much as 3.61% of cane sugar. The cane sugar is quickly inverted and we have only a little more than 0.5% of cane sugar in the overripe stage.

From the results obtained in this investigation the following conclusions may be drawn:

First, that there is a gradual diminution in the acidity of this fruit during the ripening period and at the same time there is a more pronounced increase in the amount of reducing sugar formed.

Second, the greatest increase in total sugars occurred in passing from the unripe to the ripe condition.

Third, that cane sugar plays a very important part in the ripening of this fruit, and the idea is suggested that a fruit is just ripe when it contains the maximum amount of cane sugar.

Fourth, that this fruit contains the enzyme invertase, which is most active in passing from the ripe to the overripe stage.

LEXINGTON, KY.

[CONTRIBUTION FROM THE ORGANIC LABORATORY, COLUMBIA UNIVERSITY, AND THE HARRIMAN RESEARCH LABORATORY. No. 260.]

THE INFLUENCE OF CERTAIN SUBSTANCES ON THE ACTIVITY OF INVERTASE.

BY EDWARD G. GRIFFIN AND J. M. NELSON.

Received December 20, 1915.

Effect of Glass Beads.—Beard and Cramer¹ have shown that glass beads have an inhibiting influence on the activity of lipase, diastase and invertase, and claim that this is due to the alteration in the concentrations, produced by altering the surface energy at the larger surface of the glass beads. They found that the effect increased with the time and also with the temperature, and that a part but not all of the activity was regained when the beads were removed.

As glass is appreciably soluble in water and gives to it an alkaline reaction, it seems probable that these results were due to a change in the hydrogen-ion concentration rather than to the surface of the beads. The following experiments serve to confirm this view:

Portions of 50 cc. of a 10% cane-sugar solution with 1 cc. of invertase solution, were placed in Non-sol glass bottles with varying amounts of glass beads, and the inversion allowed to take place.

Grams of glass beads.....	0.0	25	50	100
Conc. of H ⁺	10 ^{-5.9}	10 ^{-6.5}	10 ^{-7.1}	10 ^{-8.5}
Change in rotation in 24 hrs.....	0.34°	0.11°	0.06°	0.02°

¹ *Proc. Roy. Soc., (B)* 88, 575 (9115).

The hydrogen-ion concentration was determined by suitable indicators. It will be noticed that the hydrogen-ion concentration decreases as the amount of the glass beads increases. As Sørensen,¹ Fales and Nelson² and others have shown, that the optimum for invertase for these conditions is $H^+ = 10^{-4.4}$, and that the activity is very small at $H^+ = 10^{-8}$, it seems clear that the alkalinity from the glass beads is the cause of the effect produced.

The following results with the solutions containing 50 cc. of a 20% cane-sugar solution, 10 cc. of invertase solution and 50 cc. of one of Sørensen's "buffer solutions" confirm this view:

TABLE I.

	Grams of glass beads.	Temperature.	p_{H^+} .	Changes in rotation.		
				24 hrs.	48 hrs.	72 hrs.
A ³	100	37	4.9	1.82°	3.91°	5.03°
C ³	100	37	4.9	1.80°	3.88°	5.10°
B ⁴	20	37	6.7	1.23°	2.32°	3.14°
D ⁴	37	6.7	1.22°	2.31°	3.25°
E ⁴	100	20	6.0	0.98°
F ⁴	20	6.0	1.07°

In E and F a weaker invertase solution was used.

p_{H^+} is Sørensen's symbol for expressing the concentration of the hydrogen ion. The values are the negative exponents to which the number 10 must be raised in order to equal the given concentration. Thus $p_{H^+} = 4.5$ means that the hydrogen-ion concentration is equal to $10^{-4.5} = 0.0003$ mols hydrogen ion per liter.

These experiments show that the glass beads produce no effect either at 20° or 37° when the hydrogen-ion concentration is kept constant by means of the "buffer solutions."

After the work described was completed, the attention of the authors was called to a statement of Armstrong and Armstrong⁵ in which they suggest that the effect of the glass beads is probably due to the solubility of the glass. Since they made no measurements and Beard and Cramer still insist on their original conclusions,⁶ it seems worth while to publish these results.

Effect of Serum and Egg Albumin on the Activity.—Eriksson⁷ found that serum neutralized with very dilute hydrochloric acid inhibited the activity of invertase, and the extent of this effect was dependent on the order of mixing of the substrate, enzyme and inhibitor, and also on the

¹ *Biochem. Zeit.*, 21, 131 (1909).

² *THIS JOURNAL*, 37, 2786 (1915).

³ Buffer solution, sodium citrate and hydrochloric acid.

⁴ Buffer solution, primary and secondary phosphate mixture.

⁵ *Nature*, 95, 425 (1915).

⁶ *Ibid.*, 95, 561 (1915).

⁷ *Z. physiol. Chem.*, 72, 324 (1911).

length of time of contact of the enzyme and inhibitor before addition to the substrate. The addition of acid lowered this inhibiting effect. Hedin¹ noted that serum and egg albumin had a similar effect on the activity of rennet. Both Eriksson and Hedin attribute this retarding influence to the enzyme combining with the inhibitor in an "irreversible or slightly reversible" way, thereby causing the enzyme to become inactive.

A series of experiments, similar to those of Eriksson, was undertaken in which the particular hydrogen-ion concentration of each solution was determined, and the results obtained showed that when the latter was kept constant, no retardation occurred.

TABLE II.

	Solutions used.					
	Cc. 10% cane-sugar soln.	Cc. invertase soln.	Cc. serum soln.	Cc. water.	Cc. buffer soln.	Cc. 0.1 M HCl soln.
A ²	80	5	10	5
B ³	80	5	10	5
C.....	80	5	15 ⁴	...
D.....	80	5	..	15
E.....	50	2	10 ⁵	3.5	..	1.5
F.....	50	2	..	5	10 ⁵	...
G.....	50	2	..	15
H.....	50	2	10 ⁵	5
J ³	80	5	5	10
K ³	80	5	5	10
L.....	80	5	15 ⁴	...

TABLE III.

Solution.	A.	B.	C.	D.	J.	K.	L.	E.	F.	G.	H.
p_H^+	8.2	8.2	8.2	5.9	8.1	8.1	8.1	4.3	4.3	5.9	8.1
Change in rotation in 24 hrs.....	1.37°	1.38°	1.36°	2.19°	1.56°	1.48°	1.47°	1.74°	1.77°	1.35°	0.53°

In comparing the behavior of Solutions A and B with that of C in Table III, it becomes evident that the serum has no inhibiting influence on the rate of inversion. The values for D show that the hydrogen-ion concentration in the control solution must be the same as that of the serum solutions, if comparable results are to be obtained. The apparent retardation observed in contrasting the values of A and B with that of D is therefore not due to any influence of the serum except in so far as the serum causes the solution to become more alkaline. Eriksson was aware of the tendency of the serum to cause the solution to become alkaline, and that a change

¹ *Z. physiol. Chem.*, 60, 85, 364 (1909).

² The invertase and serum were mixed and allowed to stand for one hour at 37° before adding the rest of the solution.

³ All parts of the solution were mixed at once.

⁴ Phosphate mixture.

⁵ Citrate and hydrochloric acid.

⁶ A 25% aqueous serum solution.

in the acid or alkaline condition of the solution influenced the activity of the enzyme. In order to avoid this source of error in his measurements of the retardation, he neutralized the serum with hydrochloric acid, but apparently he did not neutralize to any particular hydrogen-ion concentration, nor did he bring the hydrogen-ion concentration of the control solution to the same value as that of the serum solution. He also states that as the serum is neutralized, the inhibiting influence of the serum diminishes, but is not completely destroyed as observed by Hedin in the case of some other enzymes. The values from Solutions E, F and H show that when the serum is neutralized with hydrochloric acid as in the case of E, the lowering of the inhibiting effect is only a question of the relative hydrogen-ion concentrations. The value from G shows further that the serum in E has an accelerating effect instead of a retarding one, due to the value of p_H^+ being 4.3, which is closer to the optimum hydrogen-ion concentration for invertase than the value of p_H^+ in G, which is 5.9. The values obtained from Solutions A and B, where the order of mixing of the serum, cane sugar, and invertase was varied, are the same, therefore nullifying this contention of Eriksson. Upon comparing the values of J, K and L with those of A and B, it is to be noted that the amount of serum used has no effect. Similar results were obtained when egg albumin was used in place of serum, as will be noticed from the results obtained in the series of experiments shown in Table IV.

TABLE IV.

The solutions used all contained besides 80 cc. of 10% cane-sugar solution and 5 cc. of invertase solution, the following amounts of:

	Cc. egg albumin.	Cc. water.	Cc. buffer soln.	Cc. 0.1 M HCl.		Cc. egg albumin.	Cc. water.	Cc. buffer soln.	Cc. 0.1 M HCl.
A.....	1	14	H.....	5	7	..	3
B.....	5	10	I.....	5	4	..	6
C.....	15	J.....	5	2	..	8
D.....	15 ¹	..	K.....	15 ²	..
E.....	15 ¹	..	L.....	15 ³	..
F.....	15 ¹	..	M.....	15 ³	..
G.....	..	15					

TABLE V.

Solution.	A.	D.	B.	E.	C.	F.	G.	H.	K.	I.	L.	J.	M.
p_H^+	9.0	9.0	9.3	9.3	9.5	9.5	5.8	6.5	6.5	4.3	4.3	3.7	3.7
Change in rotation, 3 hrs.	0.61°	0.55°	0.36°	0.37°	0.01°	0.00°	2.35°
Change in rotation, 6 hrs.	4.58°	4.62°	10.3°	10.3°	9.67°	9.69°

The amount of inversion in Solutions A, B, C and G, shown in Table V, indicate an apparent retardation of the activity of the invertase by the

¹ Sodium borate and sodium hydroxide.

² Phosphate mixture.

³ Sodium citrate and hydrochloric acid.

increasing amounts of egg albumin in the solution. The results from D, E and F, however, show that this retardation is due to the change in hydrogen-ion concentration of the solutions caused by the egg albumin, and that the presence of the latter has nothing to do with the rate of inversion. The results from H, I, J, K, L and M show that neutralizing the egg albumin with dilute hydrochloric acid has no effect outside of changing the hydrogen-ion concentration.

In order to see whether any different effect occurred when the egg albumin was allowed to remain in contact with the invertase for some time before it was added to the substrate as claimed by Hedin in the case of rennet, the following experiments were undertaken.

Three solutions were used for this purpose:

A. 15 cc. of a solution (prepared by beating together 30 cc. of egg albumin and 33 cc. of a 0.1 *M* solution of hydrochloric acid and then making up to 100 cc. with water) and 5 cc. of an invertase solution were allowed to stand for 1 hour and then added to 80 cc. of a 10% cane-sugar solution.

B. The same amounts of egg albumin, invertase, and cane-sugar solutions, all were mixed at once.

C. 15 cc. of a solution containing enough of a mixture of sodium citrate and hydrochloric acid to give the same hydrogen-ion concentration as that of A and B, were added to 80 cc. of the cane-sugar solution and 5 cc. invertase.

TABLE VI.

Solution.	A.	B.	C.
p_H^+	4.5	4.5	4.5
Change in rotation in 2.5 hrs.	10.38°	10.34°	10.33°

The results show that in the case of invertase at least, it makes no difference whether or not the enzyme and the egg albumin are allowed to remain in contact for some time before being added to the substrate.

Effect of Charcoal on the Activity of Invertase.—Eriksson¹ also found in studying the influence of animal charcoal on the activity of invertase that it too, like serum and egg albumin, had an inhibiting effect, which was greater when the charcoal and invertase were mixed and allowed to stand in contact for some time before being added to the cane-sugar solution, than when all three, enzyme, inhibitor, and substrate, were mixed at once.

The experiments of Eriksson were repeated and the results obtained (Table VII) showed that in this case also it was only a question of hydrogen-ion concentration.

The values of p_H^+ for Solutions A and C, the latter especially, when compared with that of Solution E, show that the presence of charcoal does effect the hydrogen-ion concentration of the solution. When buffer was added to Solution E as in Solutions B and D, so that p_H^+ was of

¹ *Loc. cit.*

the same value as that of Solutions A and C, respectively, then the activity of the invertase was the same as can be seen by comparing the values of A with B, and C with D. The inhibiting effect of charcoal must, therefore, be attributed to a change in the hydrogen-ion concentration. The values from Solutions F, G, H, and I and their controls show that the same holds true for charcoal at different concentrations of hydrogen ion as long as p_{H}^+ is of the same value as that of the control solution. Several different charcoals were used and the results obtained, all agreed with those found in the case of the above solutions and therefore have been omitted in the table.

TABLE VII.

The solutions used contained, besides 80 cc. of 10% cane-sugar solution and 10 cc. of an invertase solution, also the following:

	Gram charcoal.	Cc. buffer solution.	Cc. water.
A ¹	0.2 ¹	..	10
B.....	..	10	..
C ²	0.2 ²	..	10
D.....	..	10	..
E.....	10
F ³	0.2 ¹	10	..
G ⁴	0.2 ¹	10	..
H ⁴	0.2 ¹	10	..
I ⁴	0.2 ¹	10	..
J.....	..	10	..
K.....	..	10	..
L.....	..	10	..
M.....	..	10	..

J, K, L and M were controls for F, G, H and I.

Solutions F-M, inclusive, contained stronger invertase.

TABLE VIII.

Solution.	A.	B.	C.	D.	E.	F.	J.	G.	K.	H.	L.	I.	M.
p_{H}^+	6.0	6.0	6.7	6.7	5.9	3.1	3.1	4.1	4.1	4.8	4.8	7.1	7.1
Change in rotation, in 5 hrs.	2.50°	2.48°	2.08°	2.11°	2.54°	9.54°	9.55°	10.47°	10.48°	10.57°	10.56°	6.97°	6.95°

In measuring the amount of inversion of the cane sugar in the above experiments, the bottle containing the reaction mixtures was thoroughly shaken and a sample removed, treated with sodium carbonate solution, and then read in the polariscope. The amount of cane sugar and invert sugar held back by this small amount of charcoal was not sufficient to make any appreciable difference in the readings. When larger amounts of charcoal were used, the adsorption of the sugar became noticeable and therefore the effect could not be measured satisfactorily.

¹ Finely powdered animal charcoal of a very good adsorbing power.

² Finely powdered animal charcoal ordinarily used in the organic laboratory.

³ The charcoal and invertase were mixed first and allowed to stand for 1 hour before adding the rest of the solution.

⁴ All parts of the solution were mixed at once.

The following experiments (Table IX) will illustrate this point. Three mixtures of charcoal, cane sugar and water were prepared by allowing 2, 5 and 10 g. of finely powdered animal charcoal to stand in contact with 100 cc. of cane-sugar solution for 18 hours with occasional shaking. Sixty cc. portions of each of these mixtures were added to solutions consisting of 10 cc. of primary potassium phosphate and 10 cc. of invertase solution and marked A, B and C, corresponding respectively to the 2, 5 and 10 g. of charcoal.

TABLE IX.

Solution.	p_H^+ .	Change in rotation after	
		0 hours.	24 hours.
A.....	4.9	0.05°	1.63°
B.....	5.0	0.10°	1.40°
C.....	5.0	0.24°	1.34°

The changes in rotation indicated in the 0 hours column are very likely due to the removal of some of the cane sugar by the charcoal during the 18 hours in which they remained in contact before the invertase was added. The values in the 24 hours column seem to indicate that in this case also some sugar might have been taken up by the charcoal, otherwise they ought to have been practically the same. No evidence for the presence of invert sugar in any of the above solutions after standing for 18 hours and before adding the invertase, could be detected by means of an alkaline copper solution.

Michaelis and Ehrenreich¹ found that invertase was adsorbed by relatively large amounts of charcoal, and although the filtrate from the charcoal and invertase solution showed no presence of invertase, the unfiltered mixture was still active.

Results obtained in this laboratory confirm those of Michaelis and Ehrenreich. It was found also that if small enough quantities of charcoal were employed, so that the effect of the charcoal on the concentration of the sugar was very small, thereby permitting the measurement of the amount of inversion, the activity of the invertase was unaffected by the charcoal.

The Effect of Aluminium Hydroxide on the Activity.—Michaelis and Ehrenreich also found invertase to be adsorbed, at least partially, by gelatinous aluminium hydroxide. Welker and Marshall² have made similar observations in the case of other enzymes. They failed, however, to indicate the particular hydrogen-ion concentration of the solutions employed. The question therefore arises as to whether the hydrogen-ion concentration of their solutions might not have been responsible for some of this change in activity. In order to settle this point, their work was

¹ *Biochem. Z.*, 10, 294 (1908).

² *THIS JOURNAL*, 35, 822 (1913).

repeated. It was found that aluminium hydroxide does remove invertase completely from its solution. If, however, the invertase is allowed to act on cane sugar, in the presence of aluminium hydroxide, just as in the case of small amounts of charcoal, it apparently has no effect on the activity of the enzyme, as will be observed from the following set of experiments:

Twenty cc. of freshly precipitated aluminium hydroxide, washed free from chlorides and ammonia and containing aluminium equivalent to 0.083 g. of aluminium oxide, were mixed with 20 cc. of invertase solution and filtered.

A. Twenty cc. of this filtrate were added to 25 cc. of a 10% cane-sugar solution.

B. This solution consisted of 10 cc. of invertase solution, 10 cc. of the above aluminium hydroxide and 25 cc. of the cane-sugar solution.

C. A control solution consisting of 10 cc. of a solution of phosphates necessary to give the proper hydrogen-ion concentration, 10 cc. of invertase solution and 25 cc. of cane-sugar solution.

TABLE X.

Solution.	p_H^+ .	Change in rotation after		
		1 hour.	3 hours.	4 hours.
A.....	6.3	0.00°	0.01°	0.00°
B.....	6.3	1.08°	2.43°	2.83°
C.....	6.3	1.07°	2.40°	2.80°

Experimental Part.

The hydrogen-ion concentrations were determined by the electromotive force method described by Fales and Nelson,¹ except where otherwise stated. In case there was any possibility of a change in the hydrogen-ion concentration during the time of inversion, the values of p_H^+ were determined at the beginning and end of the inversion.

The indicator method outlined by Sørensen proved inapplicable in the case of solutions containing colloids as serum and albumin. The values for p_H^+ obtained by means of indicators are compared with those from the electromotive-force method in Table XI.

TABLE XI.

Value of p_H^+ by the two methods.

Solution	α -Naphthylamino-azo-benzene sulphonate.	Methyl orange.	R. M. F.
and 3.5 cc. acid.....	4.7	3.4	3.0
and 2.5 cc. acid.....	5.1	3.8	3.4
and 1.8 cc. acid.....	5.3	4.4	4.0
Control solution			
and 0.8 cc. acid.....	...	3.0	3.0
and 0.4 cc. acid.....	...	3.4	3.4
and 0.1 cc. acid.....	4.0	4.0	4.0

¹ *Loc. cit.*

Five cc. containing varying numbers of cc. of 0.1 *M* hydrochloric acid and the rest water, were added to a solution consisting of 10 cc. of a 25% serum, and 50 cc. of a 10% cane-sugar solution. The control solution differed from this by having the same volume of water in place of the 10 cc. of serum solution.

All the inversions took place in Non-sol glass bottles at 37°, unless otherwise stated. The solutions were always preserved with toluene.

The invertase was obtained from yeast by the method of Nelson and Born.¹ The enzyme and substrate solutions were always warmed to 37° before mixing. The enzyme activity was stopped, and mutarotation effect due to the invert sugar was overcome by means of sodium carbonate as recommended by Hudson,² except in the case of solutions containing serum or egg albumin. When the latter were present, it was not necessary to add the sodium carbonate, since the reagent added to remove the protein seemed to have the same effect.

The serum and egg albumin in most cases were removed from the solutions before the latter were examined in the polariscope, by a slight modification of the method suggested by Kumagai.³ Ten cc. of the solutions were introduced into a 150 cc. Erlenmeyer flask containing 18 cc. of a 10% sodium acetate solution. Two cc. of a ferric chloride solution were then added and the mixture heated on the water bath for six minutes and filtered hot. The clear filtrate was allowed to cool and its rotation determined.

The serum used in these experiments was prepared by centrifuging fresh, defibrinated sheep's blood.

NEW YORK, N. Y.

NEW BOOKS.

A Text-book of Inorganic Chemistry. Edited by J. NEWTON FRIEND. Vol. VIII. **The Halogens and Their Allies.** By GEOFFREY MARTIN AND E. A. DANCATER. Pp. xviii + 337. Philadelphia: Lippincott, 1915. Price, \$3.00.

In order of publication, this is the second volume of the nine into which this text-book is divided (for review of Vol. I, see *THIS JOURNAL*, 37, 1641 (1915)). In many ways, the high standard of the first volume is maintained. After a concise introduction, the halogens and manganese, and their compounds with the nonmetallic elements, are described. Numerous references to the literature are given. Manufacturing processes are discussed in detail, with figures of the plant used. The familiar lecture experiments are also fully described, and are illustrated by cuts. Numerical data are abundant and appear as a rule to be judiciously se-

¹ *THIS JOURNAL*, 36, 393 (1914).

² *Ibid.*, 30, 1564 (1908).

³ *Biochem. Z.*, 57, 380 (1913).

lected as well as complete. In this volume, however, the high standard of accuracy, completeness, theoretical knowledge, and sound chemical sense, attained in the first volume, is by no means maintained. Thus sulfuric acid is reduced by hydrogen iodide to sulfur dioxide instead of to hydrogen sulfide, and potassium iodide performs the feat of acting upon phosphoric acid to give K_3PO_4 . In connection with the union of hydrogen and iodine, no data are given, and the valuable quantitative work of Bodenstein, with its interesting conclusions as to the reversal of the sign of the heat of reaction, is not mentioned. It is also stated that iodine unites directly with sulfur, selenium and tellurium, although at least four investigations have shown that iodine and sulfur form neither compounds nor solid solutions, and only tellurium forms an iodide. The most serious defects are in the sections on chlorine. The fact that in the action of chlorine on water hydrochloric acid and hypochlorous acid are formed is indeed mentioned, but the extent of the reaction is not described. On the contrary, chlorine bleaches by forming nascent oxygen and light liberates this oxygen, but has no effect on chlorine hydrate. Surely the point of view, that hypochlorous acid is decomposed by light, and is not present in chlorine hydrate, if mentioned, would have cleared up this mystery. The authors even seem to think that hypochlorous acid is a myth, for they speak of the solution of chlorine monoxide as "what is known as hypochlorous acid," and as something that "must be regarded as an aqueous solution of $HClO$." Naturally, therefore, they do not perceive that, in the distillation of dilute hypochlorous acid, the strongest solution comes off first, because the Cl_2O is expelled. Again, the fact that chlorine monoxide, when led into hydrochloric acid, gives chlorine gas, is stated without the explanation that hypochlorous acid is formed and that the latter reacts vigorously with hydrochloric acid to give chlorine. Bleaching powder is given as a mixture of two salts, instead of a mixed salt, and the various ways of obtaining hypochlorous acid from it, such as by adding half an equivalent of nitric acid, or by treating calcium carbonate with chlorine water, or by leading excess of chlorine into bleaching powder suspended in water, are stated without explanation, and the two last are accompanied by uninformative equations, in which chlorine instead of the acids is the active substance. Finally the fact that a given weight of chlorine in the form of hypochlorous acid has twice as much bleaching power (*sic.* capacity is intended) as the same weight of chlorine in bleaching powder is "explained" by equations which avoid the real explanation. In a descriptive reference book, bare facts may be given, but this work claims to be a text-book, and a text-book must be coherent and rationalized. The remaining seven volumes are all by different authors, so that it is to be hoped that, in quality, these will resemble Volume I rather than Volume VIII.

ALEXANDER SMITH.

Ueber das periodische System der chemischen Elemente. By ALOIS BILECKI. Buchholz & Diebel, Buchdruckerei J. Feitzinger, Troppau, 1915.

This is a brief treatise of 21 pages concerning an always interesting topic. The author points out the lacks in the tabular presentations of the periodic system and prefers the well-known Crookes double helix, modifying this curve somewhat. He finds that a number of elements have atomic weights which are approximately whole multiples of the number 1.86 (which he calculates as half the "theoretical atomic weight" of helium, based on the atomic weight of xenon and the losses by emanation of radioactive elements), and he indicates other approximately constant differences in other groups of elements. At the end is an appendix presenting useful tables and plates depicting some of the properties of the elements recorded and plotted in relation to their atomic weights. He is apparently unfamiliar with some of the earlier work of others,¹ but considering the enormous amount which has been written on this subject, this is not surprising.

T. W. RICHARDS.

Handbuch der Mineralchemie. Bd. II, 8, Bogen (21-30). By DORLTER, *et al.* Dresden and Leipsic: Theodor Steinkopff. Price, M. 650.

A treatment of the alkali aluminosilicates, the most important of which are the alkali members of the feldspar and mica groups. Important as the micas are, the chemical knowledge of them is tremendously hampered by their complexity, so that, while no little labor has been expended in the study of them, the data on their syntheses and alterations are often unintelligible. Without any guiding hypothesis which may serve, even temporarily, to unify the material, it seems perfectly clear to the reviewer that the only sound method an editor can follow is to make the text concise and append a complete bibliography. But here, and quite frequently in other portions of this book, diffuseness in writing and looseness in construction are the rule. The reviewer confesses to repeated efforts to extract the wheat from the chaff, but even one deeply interested in the subject rarely reads one of these volumes without a feeling of aimless floundering in a hopeless jungle.

E. T. ALLEN.

Electrische Spectroanalyse Chemischer Atome. By J. STARK. Leipzig: S. Hirzel. Price, M. 6.

The discovery was made by Stark, and independently by Lo Surdo that the hydrogen lines broke up into groups when the glowing gas was subjected to the powerful electrical field of a specially designed vacuum tube in a manner analogous to the splitting up of lines in a magnetic field (Zeeman effect). The effect has been found for only a very few elements at the present time, however. Prof. Stark's book gives a history of the discovery and a very complete account of such observations as have

¹ "The Faraday Lecture of 1911," *J. Chem. Soc.*, 99, 1214 (1911), etc.

been made up to the present time. It is, in brief, a comprehensive monograph on the Stark-Lo Surdo effect, and has little or nothing to do with chemistry.

R. W. WOOD.

A Handbook of Colloid Chemistry. By DR. WOLFGANG OSTWALD. English translation from the third German edition by Dr. Martin H. Fischer, assisted by Dr. Ralph E. Oesper and Dr. Louis Berman. Philadelphia: P. Blakiston's Son & Co. 275 pp. Price, \$3.00 net.

This work of the younger Ostwald was the most complete work on colloids we had yet seen. It dealt with the subject in a typically German scientific manner. The whole field was divided into many parts and each part was thoroughly considered by itself.

The translation is a good one. After a general description of the colloid state, there follow chapters on the relation between the physical state and other properties, on the energetics problems, on the concept of colloid chemistry, and there are two very complete chapters on mechanical or physical properties of colloid systems, such as osmotic effects, Brownian movement, diffusion, electric migration, dialysis, etc. Probably the best feature of this work, compared with others on the subject, lies in the introduction of the energy concepts to the colloid state, particularly with reference to surface-tension effects.

The translation will doubtless bring the material so thoroughly collected and digested by Ostwald within the ken of American investigators in widely different parts of natural science. The work, as written, does not appear the particular narrow province of the chemist, but belongs obviously to the physicist, biologist and scientist in general. It is only to be regretted that so long a delay was necessary for an English translation—seven years. It is a reflection on us Americans that we do not show more ready appreciation of foreign work, but we owe the translators a debt of gratitude that we now have this recognized text-book on the subject.

W. R. WHITNEY.

The Rare Earths, Their Occurrence, Chemistry and Technology. By S. I. LEVY, B.A., B.Sc., A.I.C. Longmans, Green & Co., 1915. Pp. 342, v-xiv. Price, \$3.00 net.

"The present work is intended to give a general but fairly comprehensive account of the rare earth group. In accordance with general usage, the elements zirconium and thorium have been included, though these are now recognized as falling outside the limits of the rare earth group proper." Titanium is also included, and substantial reasons for such inclusion are given.

With some judgment the work has been divided into three parts (see below), but in view, "however, of the occurrence of considerable quantity of monazite within the British Empire, * * * * * stress has been laid on the technical aspect, * * * especially developed as regards the production of monazite and the incandescent gas mantle industry * * *."

The preface indicates some special pleading. This, however, is not to be found fault with, especially if it promotes Sir Boverton Redwoods' ante bellum "Wake Up England" idea, for in spite of the brilliant individual investigations on the "submerged third" by the distinguished British *savants*, the Empire has shown in reflected light as far as the industrial development of the rare earths is concerned.

For a "hurry-up job," the work has been pretty well done, but of course such carries with it certain blemishes (pp. 221 and 243). Temperature factors have been ignored in places (p. 252) and lack of knowledge of original publication is shown in some instances (p. 253, metallic thorium).

The three parts are: (1) occurrence, which is concerned with the nature of the minerals and their mode of occurrence; (2) the chemistry of the elements, wherein the general properties and methods of separation of the different groups are considered; (3) technology, which takes up the incandescent mantle industry involving the treatment of monazite, the manufacture of mantles from cotton and ramie and artificial silk, its production and use in the mantle industry. The work ends with a consideration of the other technological uses of the cerium and yttrium elements, zirconium and thorium, with the industrial applications of titanium and its compounds.

A short introduction by the renowned Sir William Crookes gives the book a stamp of authority. It is certainly a clear exposition of the "Rare Earths" in English, if one keeps in mind the reservation animadverted. One could not but wish that it had partaken somewhat less of some foreign characteristics of certain European nations in neglecting work done in America.

The point in nomenclature, *re* titanous and titanic compounds, referred to on p. 226 is well made and prompts the reviewer to call attention to doing away entirely with the terms *-ous* and *-ic* in all chemical literature. The use of such terms is effete. Why not say titanium dichloride, trichloride, tetrachloride? Iron dichloride and iron trichloride?

Every library of chemistry should have a copy of this book.

CHAS. BASKERVILLE.

The Rare Earth Industry. By SYDNEY J. JOHNSTONE, Senior Assistant, Scientific and Technical Department, Imperial Institute, London. Royal Octavo XII. 136 pp. 42 illustrations. New York: Appleton & Company. Price, \$3.00 (7s, 6d, net).

This interesting book is the second of a series of six Manuals of Chemical Technology issued by the Appletons and edited by Geoffrey Martin. The object of these Manuals, as the editor expresses it, is "to give concise but sufficient information concerning the manufacture and utilization of certain chemical products, whose exploitation has been hitherto but little developed in this country" (England). Eight chapters cover the following

subjects: The Thorium and Cerium Industry, Titanium, Zirconium, Tantalum and Niobium, Tungsten, The Incandescent Glow Lamp Industry, Uranium and Vanadium; while a ninth chapter by Alexander S. Russell upon the Industry of Radioactive Substances completes the volume.

The author has succeeded in his purpose of making the book to be "essentially of a practical nature," and has wisely confined himself to the industrial applications of the Rare Earths, and has only dealt with the pure chemistry of these substances to a sufficient extent to insure a proper understanding of the nature and properties of the materials dealt with. The explanation for including these various elements under the head of "Rare Earths" is that it is almost impossible to discuss their utilization in a satisfactory manner without including some account of certain other metals, which are even now technically related, and the reader will be in hearty sympathy with this classification. Each chapter contains a very satisfactory bibliography which shows the extensive literary research of the author, together with a valuable classified list of the English patents upon each subject.

The chapters on the Thorium and Cerium Industry, and Tungsten and the Incandescent Electric Lamp Industry are particularly valuable and extremely well written. They deal with these respective subjects quite comprehensively from the preparation of the ore to the finished product; and while the description of the mantel-making industry is decidedly colored with the English point of view and practice, it is nevertheless extremely interesting. Both these chapters give detailed costs of manufacture, which add materially to their value. The 42 illustrations are all found in these chapters and they are extremely well chosen, describing principally apparatus and manufacturing processes. The chapter on Radioactive Substances treats this subject in a very complete manner—both historically and scientifically, as well as technically. This chapter is from the pen of Mr. Alexander A. Russell, and very appropriately closes this interesting and practical manual.

H. S. MINER.

Air, Water, and Food, from a Sanitary Standpoint. By ALPHEUS G. WOODMAN AND JOHN F. NORTON. Fourth edition, revised and rewritten. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Limited, 1914. 248 pp. 17 illus. Price, \$2.00.

Since the third edition of this work, one of the authors, Mrs. Ellen H. Richards, has died and a change of authorship is noted in the fourth edition. The book has been thoroughly revised and brought up-to-date, many parts of it being entirely rewritten to include the results of recent investigations and to present the point of view regarding some phases of the subject which has been brought about since the earlier editions.

The chapter on air and that on ventilation in the previous edition have been combined in this edition into one chapter entitled "Air and Health,"

and the subject matter has been entirely rewritten to include the more recent contributions to this important subject. In the chapter on analytical methods for air, more emphasis has been laid upon the determination of humidity and dust, and the descriptions of some of the older methods which have largely fallen into disuse have been omitted.

The chapter on the relation of water to health has been entirely rewritten and brought up-to-date, especially with reference to the bacteriological aspects of this question. The analytical methods for water have been revised and some modifications and improvements made; a somewhat more logical order has been followed in describing the different methods. More detailed explanations are given of some of the reactions involved. Short paragraphs on the bacteriological examination of water and sewage have been added, as have descriptions of the methods for determination of sulfates and putrescibility.

Under the analytical methods for food, the subject matter relating to milk has been entirely rewritten. New material has been added on the variation in composition of milk, some of the analytical methods have been omitted and others have been greatly modified. Comparatively little change has been made in the analytical methods for other foods, but in some instances new methods have been added and slight modifications of others have been made.

Some changes in the arrangement of the tables have been made. The bibliography also has been extended and brought up-to-date.

H. L. LANG.

Journal of the Association of Official Agricultural Chemists. Published Quarterly for the Association by the Williams and Wilkins Company, Baltimore. Five dollars per annum for non-members.

This journal, the first number of which has recently appeared, fills a place of importance in the literature of agricultural chemistry; the need for it has been felt for many years. It offers a proper medium for the publication of a large amount of matter which could not well be given space in any one of the existing journals, but which is of the highest interest and importance to chemists connected with experiment stations or food control laboratories.

Official methods of analysis, revised from year to year, find a place here as will also the reports of the proceedings of the annual convention of the Association of Official Agricultural Chemists. There are also reports from other official laboratories and it is probable that cities as well as the states will find this the most convenient organ for the publication of work relating to municipal control.

The journal is well printed on heavy paper; the numbers which are out make a good impression.

J. H. LONG.

THE JOURNAL

OF THE

American Chemical Society

with which has been incorporated the

American Chemical Journal

(Founded by Ira Remsen)

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 102.]

THE FREE ENERGY OF HYDROCHLORIC ACID IN AQUEOUS SOLUTION.

By JAMES H. ELLIS.

Received February 1, 1916.

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1. Purpose and Outline of the Investigation.

The fact that the laws of perfect solutions, which are conformed to by un-ionized or slightly ionized substances in dilute aqueous solutions, are subject to large deviations in the case of largely ionized substances (salts, strong acids and bases), even at small concentrations, makes it necessary, in the absence of any theoretical explanation of the deviations, to treat dilute solutions of these substances like concentrated solutions of other substances, namely, to determine experimentally the behavior of the separate substances, with the hope that this empirical study may

then lead to generalizations. Now the most important characteristic of ionizing substances is the chemical activity which results from their ionization, or more specifically the (mass action) effect which their ions exercise in determining chemical equilibria. This effect in the case of theoretically perfect solutes is proportional to the concentration of the ions, but in the case of deviating solutes there must be substituted for it a new quantity which may be regarded as the "effective ion concentration" and which has been appropriately called by Lewis¹ the activity of the ions. This quantity has been shown by Lewis to be thermodynamically related to various other properties of solutions, thereby on the one hand increasing its practical significance and on the other affording various means of evaluating it.

The most general of these thermodynamic relations, one, indeed, which may well be regarded as the best practical definition of activity is that afforded by the equation $F_1 - F_2 = R T \log(a_1/a_2)$, in which R is the perfect-gas constant and $F_1 - F_2$ represents the decrease in the free energy of the system attending the transfer at the absolute temperature T of one mol of any substance (for example, of an ion) from a solution of any concentration in which its activity is a_1 to another solution of any concentration in which its activity is a_2 ; the free-energy decrease, hereafter denoted by $-\Delta F$, being defined in general to be equal to the maximum work W producible by the change in the state of the system under consideration, diminished by the attendant increase in the product of its volume and pressure (that is, $-\Delta F = W - (p_2 v_2 - p_1 v_1)$).

The most direct way of determining the free-energy decrease attending the transfer of ions from one concentration to another, and thereby their relative activities, is the measurement of the electromotive force of cells in which such a transfer takes place; and it is with such a study of the ions of hydrochloric acid that this investigation deals. Namely, measurements have been made of the electromotive force at 18, 25, and 35° of cells of the type, H_2 (gas), HCl (at any concentration c), Hg_2Cl_2 (solid) + Hg . The change in state when one faraday passes through such a cell is



and the product of the electromotive force into the value (\mathfrak{F}) of one faraday in coulombs is equal to the free-energy decrease in joules which attends this change in state. The changes in state in two cells in which the concentrations are c_2 and c_1 differ only in the respect that the hydrochloric acid is produced at these different concentrations, and the difference ($E_2 - E_1$) in their electromotive forces multiplied by \mathfrak{F} therefore equals the free-energy decrease ($-\Delta F$) attending the transfer of 1 HCl

¹ In regard to the concept of activity see G. N. Lewis, *Proc. Am. Acad.*, 37, 49 (1901); 43, 259 (1907), and *Z. physik. Chem.*, 38, 205 (1901); 61, 129 (1907).

from a solution where its concentration is c_1 to a solution where its concentration is c_2 .

From the free-energy decrease attending the transfer of 1 HCl is then calculated the ratio $a_1^{\text{H}^+} a_1^{\text{Cl}^-} / a_2^{\text{H}^+} a_2^{\text{Cl}^-}$ of the products of the activities of the two ions of the acid at the two concentrations by means of the equation $-\Delta F = R T \log \frac{a_1^{\text{H}^+} a_1^{\text{Cl}^-}}{a_2^{\text{H}^+} a_2^{\text{Cl}^-}}$, which is based on the general definition of activity. The simplifying assumption that the two ions have equal activities in the same solution (that is, that $a_1^{\text{H}^+} = a_1^{\text{Cl}^-}$ and $a_2^{\text{H}^+} = a_2^{\text{Cl}^-}$) is then made provisionally; and the activities so calculated are compared with the ion concentrations given by the conductance ratio with a view of throwing light on the deviation of the activity of these ions from the ion concentrations commonly assumed.

This research has been carried on with the coöperation of Professor A. A. Noyes and with the aid of the grant made to him by the Carnegie Institution of Washington. The preliminary experiments were made jointly with Dr. Louis Weisberg and the final measurements with Mr. Frank W. Hall. For all this assistance I wish to express my great indebtedness.

2. Review of Previous Investigations.

Tolman and Ferguson¹ have already made measurements with hydrogen-calomel cells of the kind here described at 18° and at HCl concentrations 0.1, 0.02, 0.01, and 0.002 *N*. It seemed, nevertheless, desirable to take up these measurements anew in the hope of securing more accurate results and for the sake of extending the measurements to higher concentrations and other temperatures. Jahn² has also measured at 18°, apparently with great accuracy, the electromotive force of concentration cells of the type $\text{Ag} + \text{AgCl}, \text{HCl}(c_1), \text{HCl}(c_2), \text{AgCl} + \text{Ag}$ with the concentrations varying from 0.033 to 0.00167. From these electromotive forces can also be calculated with the aid of the transference numbers of the ions the free energy attending the transfer of 1 HCl from one solution to another.

Dolezalek³ has measured the electromotive force at 30° of hydrogen-chlorine cells with concentrated hydrochloric acid as electrolyte, thus determining directly the free energy of hydrochloric acid in solutions 5 *N* to 12 *N*. He has also determined the partial vapor pressure at 30° of hydrochloric acid in these concentrated solutions. Gahl⁴ has also made similar vapor-pressure measurements at 25°.

Other accurate electromotive measurements from which the free energy

¹ THIS JOURNAL, 34, 232-246 (1912).

² *Z. physik. Chem.*, 33, 545-576 (1900).

³ *Ibid.*, 26, 334 (1898).

⁴ *Ibid.*, 33, 178 (1900).

of transfer of univalent electrolytes can be derived are those of Jahn made with potassium chloride and sodium chloride in the same way as with hydrochloric acid, and those of MacInnes and Parker.¹ The last-named investigators measured at 25° concentration cells with silver-silverchloride electrodes and potassium chloride as electrolyte at concentrations 0.5 to 0.001 *N*, and also cells of the type $\text{Ag} + \text{AgCl}, \text{KCl}(c_1), \text{KHg}, \text{KCl}(c_2), \text{AgCl} + \text{Ag}$, for concentrations between 0.5–0.005 *N*.

Recently S. J. Bates² has published a study of the most accurate freezing-point data available, from the results of which the free energy changes attending changes in concentration of largely ionized substances can be readily derived.

The results of these investigations will be considered later in connection with the new ones to be here presented.

3. Description of the Experiments.

(a) **Preparation of the Substances and Solutions.**—The mercury for use in the cells was purified by first electrolyzing it as the anode in a 2% solution of nitric acid, stirring both the mercury and the solution well, and using a current-density of 0.005 ampere per square decimeter, in the manner recommended by Wolff and Waters.³ Electrolysis was continued for thirty hours, but six hours before its completion the mercury had ceased to tail. After this process the mercury was dried and twice distilled at a pressure of 30 mm. in a current of air. At the end of the second distillation no visible residue was left in the distilling flask. The mercury thus prepared preserved a mirror surface indefinitely.

The calomel first used in making the calomel electrodes was Kahlbaum's best product; but it did not give reproducible results. Calomel prepared by precipitation from a mercurous nitrate solution made by dissolving pure mercury in pure nitric acid was then tried. This also proved unsatisfactory, although great care was taken in its preparation. Finally, satisfactory calomel was secured by an electrolytic process analogous to that suggested by Wolff and Waters⁴ for the preparation of mercurous sulfate for standard Weston cells. Pure mercury, placed in a large clean beaker, was covered with pure 1 *N* hydrochloric acid. Both the acid and mercury were kept well stirred by a glass stirrer. The mercury was made the anode; and the cathode consisted of a piece of clean platinum foil contained in another beaker filled with hydrochloric acid and connected with the first beaker by a siphon tube. On passage of the current the mercury surface became covered with a thin film of calomel; and, as this was swept away by the stirrer, it was re-formed continually.

¹ *THIS JOURNAL*, 37, 1445–1461 (1915).

² *Ibid.*, 37, 1423–1445 (1915).

³ *Bull. Bur. Standards*, 3, 625 (1907).

⁴ *Ibid.*, 3, 631 (1907).

Various rates of stirring and various current densities ranging from 2 amp. to 0.2 amp. per sq. dm. were used, without affecting the electromotive properties of the product. The product was always of a moderately dark gray color, due to the presence of a large amount of finely divided mercury in the form of globules of diameter 0.3 mm. and less. Under the microscope, however, the calomel particles were visible as a perfectly white, amorphous, flocculent substance. Stirring was always continued for four hours after the electrolysis was terminated, in order to enable the precipitated calomel to come into equilibrium with the solution. The calomel prepared in this manner was transferred to a clean bottle and preserved under the mother liquor of the electrolysis. When tested for mercuric chloride it gave no reaction for it.

All water used in making up the solutions had a specific conductance less than 10^{-6} reciprocal ohms. It was preserved in resistance glass bottles.

Hydrochloric acid was prepared by redistilling the best commercial acid, retaining only the middle portion. The constant boiling acid thus secured was diluted with conductivity water in resistance-glass bottles to approximately 2 *N*, and analyzed by precipitating it with silver nitrate and weighing the silver chloride. Solutions of less strength were prepared by diluting a known weight of this acid with a known weight of water.

Hydrogen for the hydrogen electrode was prepared by the electrolysis of sulfuric acid solutions; it was washed before being admitted to the cell by passing it through a solution of potassium bichromate in strong sulfuric acid, alkaline pyrogallate solution, and a hydrochloric acid solution of the same temperature and concentration as that in the cell. In the preliminary work the hydrogen was also passed through a tube containing a platinum spiral at a dull red heat; but this precaution was found to be unnecessary.

(b) **Description of the Cell.**—The cell consisted, as shown in the figure, of two half cells containing the hydrogen and calomel electrodes, respectively. These half cells are shown in Figs. 1 and 2.

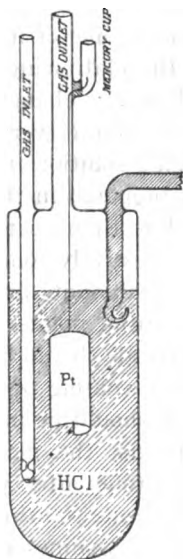


Fig. 1.

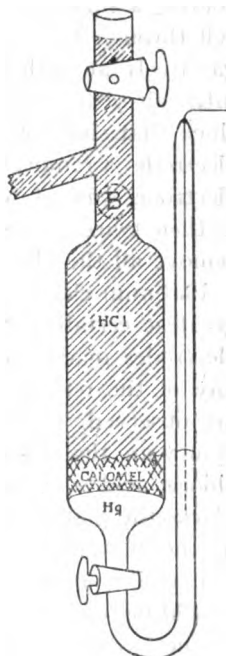


Fig. 2.

The hydrogen half cell contained sometimes two or four platinum electrodes and at other times only a single one. The electrodes were completely covered by the solution; and connection was made to them through platinum wires leading to mercury cups outside the cell. The portion of these wires within the cups was well amalgamated by electrolysis in a mercurous nitrate solution. The platinum electrodes were of thin foil and had a surface of 15 sq. cm. They were cleaned, before the cell was made up, by fusion with potassium acid sulfate, followed by careful washing in boiling water. After introduction into the cell they were heavily coated with platinum black.

Hydrogen was bubbled into the cell through a small capillary opening designed as shown in the figure, so as to give a large number of small bubbles. It escaped through an exit tube at the top of the cell. This exit tube was covered with a cap ending in a capillary bend into a hook. The tube by means of which liquid connection is established with the calomel cells also has a hook at its lower end, to prevent gas bubbles from entering it and interrupting the column of liquid.

The platinization of the platinum foil is of importance. Clean foil must be employed, and the platinizing solution should consist of pure chloroplatinic acid (containing 1% Pt). The addition of lead to secure a better coating of platinum black is objectionable. To deposit the coating a small auxiliary electrode of platinum foil is introduced into the cell through the hydrogen exit tube, and a current sufficient to liberate gas freely at both electrodes is passed. This current is commutated at intervals of five minutes for two hours or more, or until the coating is so thick that shaking causes some of it to fall off, after which the auxiliary electrode is removed, the platinizing solution poured off, and the coated electrode washed with many changes of conductivity water. The cell is then twice allowed to stand overnight full of conductivity water, to remove all the platinizing solution from the coating.

Platinum electrodes prepared in this manner are reproducible with the greatest certainty to less than 0.01 millivolt; and out of eight or ten electrodes made up successively, one is rarely found which differs from any of the rest by this amount, provided the precautions given above are observed. The essential points in securing reproducibility and constancy are that the electrode should be completely immersed in the hydrochloric acid solution, the coating of platinum black should be thick and black, the platinum foil should be initially clean, no lead should be used in the platinizing solution, the platinizing salts should be completely removed from the electrode after platinizing, and sufficient hydrogen should be fed to the electrode to insure saturation with the gas.

The hydrogen electrode assumes its equilibrium value within three or four hours after the passage of hydrogen is commenced; it functions as an

oxygen electrode until the oxygen initially present upon it is displaced by the hydrogen. If the bubbling of hydrogen through the solution is reasonably continuous (a few bubbles every few seconds) and if the coating of platinum black is sufficiently thick, no variation whatsoever in the electromotive force of the electrode can be observed even with a very sensitive potentiometer. The electrode is quickly responsive to changes in barometric pressure; and it is possible to detect readily a change of one millimeter in the barometric height by observing the electromotive force of the hydrogen electrode. To test quantitatively the response of the hydrogen electrode to changes in hydrogen pressure, the hydrogen in one cell containing approximately 0.1 normal acid at 25° was subjected to a pressure of 38.5 cm. of mercury in excess of the atmospheric pressure, and the change of electromotive force observed. The figures given in Table I were obtained.

TABLE I.—RESPONSE OF THE HYDROGEN ELECTRODE TO CHANGES IN PRESSURE.

Elapsed time.		Barometer. Cm. Hg.	Excess pressure. Cm. Hg.	Electromotive force. Volt.
Hr.	Min.			
	0	...	0.0	0.40069
	16	...	0.0	0.40074
1	37	...	0.0	0.40081
2	5	76.90	0.0	0.40081
Excess pressure then applied.				
2	20	76.90	38.5	0.405
2	28	76.90	38.5	0.4058
2	32	76.90	38.5	0.40602
2	41	76.90	38.5	0.40613
2	56	76.90	38.5	0.40625
3	18	...	38.5	0.40622
3	29	76.85	38.5	0.40618
3	56	76.85	38.5	0.40616
4	35	76.85	38.5	0.40623
4	55	76.77	38.5	0.40623
Excess pressure then removed.				
5	7	76.77	0.0	0.40105
5	7	76.77	0.0	0.40097
5	21	76.77	0.0	0.40085
5	29	76.77	0.0	0.40085
5	39	76.77	0.0	0.40085
5	45	76.72	0.0	0.40087

It will be seen from this table that, before the pressure was applied, the electromotive force was constant at 0.40081 volt, that it rose to an approximately stationary value of 0.40623 volt in an hour or so after the excess pressure was applied, and that within an hour after the excess pressure was removed the electromotive force fell to a stationary value of 0.40085 volt. If this latter value is corrected for the change in barometric

pressure from 76.90 to 76.72 cm. remembering that 1 cm. increase in the pressure corresponds for small pressure changes to an increase of 0.00017 volt in the electromotive force, it is found that, had the barometer not changed, the final value would have been 0.40090 volt. Although this value differs by 0.00009 volt from the initial value, the agreement is fairly satisfactory considering that these measurements were made in the early stages of the work, when neither the hydrogen nor the calomel electrode had been gotten well under control. The mean of the two values is 0.40086 volt, and the rise in electromotive force to 0.40623 thus means a rise of 0.00537 volt. If the rise to be expected is calculated by means of the formula $E_2 - E_1 = (R T / 2F) \log (p_2 / p_1)$, remembering to subtract from the recorded values of the pressures the pressure of aqueous vapor at 25°, the figure 0.00536 volt is obtained. There is thus good evidence that the hydrogen electrode acts in a reversible manner; and the data given above show that it responds quickly both to increase and to decrease of the hydrogen pressure.

After passage of hydrogen for thirty-six hours to thoroughly saturate the solution and electrode, several hydrogen half cells were sealed by drawing down the entrance and exit tubes for the hydrogen with a hand blast lamp. These cells maintained their electromotive force constant within one millivolt for about a week, but showed that, for an accuracy of 0.1 millivolt or better, it is essential to have a continual supply of hydrogen pass through the solution, thus making it impracticable to construct a standard cell with a hydrogen electrode.

It should also be mentioned that, if the entrance of mercury ions from the calomel electrode into the hydrogen half cell is prevented, the coating of platinum black apparently retains its effectiveness indefinitely. In the present work electrodes were used for a period of six months without showing any need of replatinization. On the other hand, if the hydrogen and calomel electrodes are not effectively separated, as they were not in the first stages of this work, nor in the work of Tolman and Ferguson previously referred to, the coating of platinum black becomes gray from deposited mercury within a few days, and cells containing such electrodes give results which may be low by 0.1 millivolt or more.

The type of calomel half cell employed is shown in Fig. 2 on page 741. It dispenses with the use of a platinum leading-in wire sealed through the glass, a mercury column taking its place. This is a distinct advantage; for such wires, even if well amalgamated originally, appear to become coated with a crust of solid matter if allowed to come into contact with the calomel, and they ultimately fail to make good contact with the mercury button in the bottom of the cell. Connection with the mercury column of my cells was made with an amalgamated platinum wire, it is true, but in such a way that no calomel could touch the wire.

Because of the lesser degree of reproducibility of the calomel electrodes four distinct calomel half cells were always made up. These were connected with one another by a horizontal tube indicated by the circle B in the figure.

Before charging the cell the calomel was shaken for two days or more with successive portions of hydrochloric acid of the concentration to be used, to bring it into equilibrium with the acid. The cell was then charged with the proper amount of this calomel and with the acid with which it had been shaken, the stopcocks were closed, the tube subsequently to be sealed to the tube coming from the hydrogen cell was closed with a glass plug and rubber connector, and the whole cell was rotated end-over-end for at least three hours to ensure perfect equilibration. This is essential, and it should be emphasized that, in order to secure reproducible electrodes, one must not allow any hydrochloric acid which has not been saturated with calomel in the manner just described to enter the cell.

Calomel electrodes prepared with these precautions assume (except when the acid is more dilute than 0.03 *N*) their true potential within thirty minutes after coming to the temperature of the thermostat in which they are placed, and then remain constant. But, unless the precautions are observed, the cells do not come to a steady value even after several days, and they show small capricious variations from second to second, which are greatly magnified by shaking the cell. Electrodes correctly prepared are reproducible to within 0.04 to 0.05 millivolt, and do not change their value on shaking, while electrodes prepared without thorough equilibration may be expected to vary from one another by a whole millivolt, and to change their value on shaking even after they appear to have come to a steady value. Indeed, the constancy of an undisturbed calomel electrode is no indication whatsoever of the satisfactory performance of the electrode; for, even when an electrode has not been rotated, it settles down to a steady value in the course of a few days, although this value may be as much as a millivolt (or even ten millivolts) removed from the correct value. It should be assumed that the electrode is acting satisfactorily only when a number of electrodes prepared simultaneously or at different times give substantially the same electromotive force, when these electrodes are steady in their values and not sensitive to shaking, when they show no tendency to polarize in ordinary use with a potentiometer, and when they exhibit no temperature hysteresis. All the electrodes used in the present investigation fulfilled these conditions.

It may be incidentally mentioned that the common practice of bringing electrodes into agreement by allowing them to stand connected together in the same solution does not afford evidence that the electrodes have

become really identical; for by this treatment inherent differences in the electrodes may have been merely temporarily compensated by concentration changes automatically produced in the porous material upon their surfaces.

The complete hydrogen-calomel cell possessed nearly the steadiness of a cadmium standard cell. No variation in its electromotive force from instant to instant could be observed with a potentiometer reading to 0.01 millivolt, and the variations observed in the course of several days almost always agreed with those predictable from the changes in the barometric pressure and the slight temperature changes in the thermostat. The following set of values (corrected for barometric changes) indicates the constancy of the cell, and shows its entire freedom from temperature hysteresis. The acid used in these measurements contained 1.9278 mols HCl per 1000 g. water.

TABLE II.—RESPONSE OF THE CELLS TO CHANGES IN TEMPERATURE.

Elapsed time.			Corrected E. M. F. Volt.	Elapsed time.			Corrected E. M. F. Volt.
Hr.	Min.	Temperature.		Hr.	Min.	Temperature.	
	0	35.00°	0.23302	3	50	18.00°	0.23767
	40	35.00°	0.23304	4	30	18.00°	0.23769
1	50	25.00°	0.23588	10	30	25.00°	0.23586
2	30	25.00°	0.23590	14	0	25.00°	0.23588

It will be noticed that this cell, which is a typical one, gave the same value at 25°, whether this temperature was approached from 35° or from 18°; and it may be stated in addition that the electromotive force of the cell appears to follow within a few minutes any temperature change.

The fact that the cells gave electromotive forces constant for days, indicates that the continued passage of hydrogen through the hydrogen half cell was accompanied by no progressive change in the concentration of the acid due to removal of water vapor.

It should be observed that the cells are satisfactory only with fairly concentrated acid. With acid of lower concentration than 0.03 *N* the calomel electrode is for some reason not at all reliable. This may be due to some change in the solid phase, such as the formation of a basic chloride or of a subchloride producing a solid solution with the original calomel. At any rate, something happens at low concentrations which affects the measurements noticeably even at 0.03 *N*, and which produces so pronounced an error at 0.01 and at 0.003 *N* as to render the measurements at those concentrations valueless.

The measured electromotive forces of the cells containing the acid at the highest concentration (4.484 molal) might be slightly in error, owing to the solubility of calomel in acid of this strength. The data determined by Richards and Archibald¹ show, however, that a 4.484 molal HCl

¹ *Z. physik. Chem.*, 40, 391 (1902).

saturated with calomel is only 0.0016 molal in HgCl_2 . The molal ratio $\text{HgCl}_2 : \text{HCl}$ is therefore only 0.035%, thus altogether too small to produce through complex formation or otherwise an appreciable change in the concentration or activity of the hydrochloric acid.

(c) **Method of Setting Up the Cell.**—The technique of preparing a hydrogen-calomel cell is somewhat complicated. The two separate half cells are first cleaned with an acid bichromate solution, and then thoroughly washed with conductivity water. The hydrogen half cell is then rinsed out several times with acid of the concentration to be used, allowing it to stand full of acid for some time between the rinsings. The calomel cells are then completely dried by passing through them a current of air filtered through cotton wool. Their stopcocks are freed from grease, and they are smeared anew with a small quantity of fresh grease. The small vertical side tubes of the four calomel half cells are then filled with pure mercury, as are also the bores of the four small stopcocks at the bottom of the cells. These stopcocks are then closed, and the tops of the side tubes are sealed off close to the top of the mercury columns with a hand blast-lamp. The tube leading to the hydrogen cell is closed by a glass plug held on by a short rubber connector. The air pressure in the cells is slightly reduced with a water pump, and acid of the proper concentration which has been equilibrated with calomel is allowed to flow in. The cell is shaken and then the acid is sucked out, this process being twice repeated. Finally, equilibrated calomel is introduced by the aid of the water pump, and enough equilibrated acid to fill the cell completely is allowed to flow in. The amount of calomel used is apparently immaterial provided it is sufficient to cover the mercury button later introduced.

The calomel half cells thus prepared are slowly rotated end-over-end for four hours or more, then shaken and tilted so as to distribute the calomel equally among the four separate cells. The sealed-off ends of the side tubes containing the mercury are then cracked off, and the stopcocks at the bottom of the cells are opened so as to allow the mercury to flow slowly into the bottom of each cell and form the mercury electrode.

The calomel half cells are now placed in the thermostat and tested for agreement with one another. If the process has been successful, as after practice it almost invariably is, the maximum variation between any two cells will not be greater than 0.05 millivolt, although occasionally with the less concentrated acids variations of 0.10 millivolt may be observed. If the calomel half cells prove satisfactory, they are sealed to the hydrogen half cell with a hand blast lamp, the two connection tubes having first been dried out with filter paper. Gentle suction is now applied at the top of the calomel half cells, enough liquid to fill the connection tube is drawn over from the hydrogen cell, and the stopcock at the top

is closed. The liquid boundary is formed at the point where the connection tube joins the vertical tube leading from the top of the group of calomel cells, and when formed in the way described there is no introduction of acid from the hydrogen cell into the calomel cell nor the reverse. After the liquid junction has been formed, the cells are replaced in the thermostat, and hydrogen is started bubbling through the hydrogen half cell. In five or six hours measurements may be commenced.

(d) **Description of the Measurements.**—The temperature variations of the thermostat seldom exceeded 0.01° . The temperature was measured to 0.01° on two Baudin thermometers (Nos. 16344 and 16862), which had been calibrated at the Bureau of Standards. Their ice points were re-determined during the course of this investigation, and found to agree within 0.01° with those determined at the time of the calibration.

The apparatus for the measurement of the electromotive force consisted of a Leeds and Northrup potentiometer (instrument No. 9043) which has been recently overhauled and put into good condition by the makers. A Weston standard cell (No. 1103) was used, which was calibrated at the Bureau of Standards during the course of the work. It was kept in a box lined with heavy felt to prevent sudden changes of temperature. A correction for thermoelectric forces in the galvanometer circuit and in the potentiometer was always made, but it amounted at most to $+0.00002$ volt. The potentiometer settings were made with an accuracy of 0.00001 volt.

After setting up the cell in the manner previously described and allowing hydrogen to bubble through it for six hours, the potentiometer current was roughly adjusted by the aid of an auxiliary sub-standard cell; and then the electromotive force of each calomel half cell against the hydrogen half cell was measured. Immediately after this the electromotive force of the standard cell was measured, giving a calibration of the potentiometer scale more accurate than if the attempt were made to adjust the scale to read directly in the usual manner. The temperature of the thermostat was then measured on the Baudin thermometers, and the barometer reading was taken. The cell was then allowed to remain one hour or more at the same temperature, and the measurements were repeated. If the electromotive forces measured at these two times checked within 0.00002 volt after allowance had been made for the change in the barometric pressure, the cell was brought to the next temperature at which it was to be measured, and the same procedure was repeated. If a check within 0.00002 volt was not obtained (which happened only once during the course of the measurements), the cell was allowed to stand for another hour without changing its temperature, and the measurements were repeated. Preliminary work on the cells gave satisfactory evidence that, if

cells kept the same value for one hour, they would in all likelihood retain it for days.

After the measurements at the three temperatures (18, 25, and 35°) were made, the cell was emptied, cleaned, and refilled for measurements with another concentration of acid.

4. The Experimental Data.

To reduce the observations to standard conditions, the following corrections were applied in the order given:

(1) The ice points of the Baudin thermometers having been re-determined and found to lie within 0.01° of the values obtained by the Bureau of Standards, the corrections determined by the Bureau were applied to the thermometer readings.

(2) The barometer readings were corrected for an instrumental error of +0.7 mm. and for the temperature of the mercury and scale with the aid of the table given in Landolt-Börnstein Tabellen; also for the variation of gravity due to the fact that the latitude of Boston is not 45°, but 42° 21'.

(3) The actual hydrogen pressure at the platinum electrode of the cell was obtained by subtracting from the corrected barometer reading the pressure of water vapor above the hydrochloric acid at the different temperatures of measurement; and then adding to this figure the mercury equivalent (0.33 mm.) of the column of liquid in the cell, measured from the middle of the platinum electrode to the upper surface of the liquid.

(4) The observed electromotive forces were treated as follows: (a) The mean of the values for the four cells was computed, and this mean was then corrected in the following manner for the error caused by the fact that the potentiometer was not accurately adjusted to be direct reading: From the value of its scale obtained each time by measuring the electromotive force of the standard cell, corrected electromotive forces of the hydrogen-calomel cell were computed by multiplying the observed electromotive force of that cell by the true electromotive force of the standard cell and dividing by the observed electromotive force of the latter. The standard cell (Weston No. 1103) was certified by the Bureau of Standards to have the value 1.01855 international volts. (b) This corrected electromotive force was further corrected by adding +0.00002 volt for the thermoelectric effects in the potentiometer. (c) The value thus obtained was corrected to what it would have been, had the hydrogen pressure in the cell been exactly one atmosphere (760 mm. mercury at zero degrees, sea-level, and 45° north latitude). This correction was made by the logarithmic formula correlating electrode potential and gas pressure: it amounted to -0.00000057 T per centimeter of mercury above 76 cm. (d) From the values so obtained the temperature coefficient of each cell was computed for different temperatures, and

corrections were made for the slight variations of the thermostat temperatures from 18, 25, and 35°.

The densities at 25° of the solutions were carefully determined, thus enabling the acid content to be expressed also in mols per liter of the solution at 25°. The values found (referred to water at 4°) are as follows:

TABLE III.—DENSITIES OF HYDROCHLORIC ACID SOLUTIONS AT 25°.

Mols HCl per 1000 g. water.	Density.	Mols HCl per 1000 cc. solution.	Mols HCl per 1000 g. water.	Density.	Mols HCl per 1000 cc. solution.
4.484	1.0654	4.1044	0.5095	1.0059	0.50345
1.9278	1.0291	1.8535	0.3376	1.0031	0.3346
1.0381	1.0149	1.0159	0.10040	0.9989	0.09999
0.7714	1.0105	0.7587	0.03332	0.9972	0.03324

The observed electromotive forces are presented in Table IV. The first column gives the temperature, and the second the pressure of the hydrogen obtained as described in Paragraph (3) above. The third column gives the time which elapsed after the first measurement was made. The remaining columns give the observed electromotive forces of the standard cell and of the four cells formed by combining the hydrogen half cell with each of the four calomel half cells. The acid concentrations are given in mols HCl per 1000 g. water, the weights being corrected for air buoyancy.

TABLE IV.—THE OBSERVED ELECTROMOTIVE FORCES OF THE SEPARATE CELLS.

Temperature.	Hydrogen pressure.	Elapsed time.	Observed electromotive forces.				
			Std. cell.	Cell I.	Cell II.	Cell III.	Cell IV.
Acid content: 4.484 mols HCl per 1000 g. water.							
24.96	74.95	0	1.01927	0.15494	0.15494	0.15494	0.15494
24.96	74.86	3:20	1.01927	0.15497	0.15497	0.15497	0.15497
35.02	73.14	5:08	1.01926	0.15085	0.15083	0.15080	0.15077
35.03	73.14	6:05	1.01926	0.15084	0.15083	0.15081	0.15078
17.81	75.62	7:35	1.01927	0.15763	0.15762	0.15763	0.15766
18.31	75.74	9:50	1.01927	0.15751	0.15752	0.15751	0.15756
Acid content: 1.9278 mols HCl per 1000 g. water.							
35.02	71.85	0	1.01931	0.23250	0.23242	0.23243	0.23244
35.00	71.85	0:40	1.01928	0.23251	0.23244	0.23243	0.23246
25.01	73.62	1:50	1.01929	0.23566	0.23559	0.23562	0.23564
25.00	73.62	2:30	1.01929	0.23567	0.23562	0.23563	0.23566
17.99	74.43	3:50	1.01926	0.23758	0.23753	0.23754	0.23757
18.00	74.43	4:30	1.01928	0.23761	0.23755	0.23756	0.23759
25.00	73.90	10:30	1.01933	0.23569	0.23564	0.23565	0.23568
25.01	73.81	13:55	1.01930	0.23569	0.23564	0.23565	0.23568
Acid content: 1.0381 mols HCl per 1000 g. water.							
17.93	74.87	0	1.02156	0.27984	0.27982	0.27978	0.27982
25.01	74.04	1:50	1.01930	0.27794	0.27789	0.27786	0.27788
25.01	74.05	2:40	1.01940	0.27793	0.27791	0.27789	0.27793
35.00	72.21	3:25	1.01921	0.27552	0.27546	0.27546	0.27551
35.00	72.21	4:00	1.01928	0.27549	0.27545	0.27544	0.27548

TABLE IV (continued).

Temperature.	Hydrogen pressure.	Elapsed time.	Observed electromotive forces.				
			Std. cell.	Cell I.	Cell II.	Cell III.	Cell IV.
Acid content: 0.77137 mol HCl per 1000 g. water.							
24.98	74.68	0	1.01919	0.29573	0.29561	0.29564	0.29570
24.99	74.63	2:10	1.01926	0.29572	0.29561	0.29564	0.29568
35.00	72.71	4:55	1.01929	0.29373	0.29369	0.29367	0.29369
35.00	72.44	7:30	1.01924	0.29373	0.29366	0.29359	0.29366
18.00	75.11	9:30	1.01922	0.29663	0.29657	0.29654	0.29662
18.01	75.09	10:35	1.01950	0.29672	0.29666	0.29663	0.29669
Acid content: 0.50948 mol HCl per 1000 g. water.							
18.00	75.08	0	1.01928	0.31921	0.31914	0.31907	0.31917
18.00	74.94	1:30	1.01926	0.31921	0.31913	0.31907	0.31918
24.96	74.06	4:55	1.01928	0.31857	0.31850	0.31846	0.31853
24.96	74.02	6:15	1.01929	0.31858	0.31851	0.31847	0.31855
35.00	72.16	7:30	1.01929	0.31726	0.31722	0.31713	0.31718
34.99	72.20	8:30	1.01929	0.31727	0.31721	0.31712	0.31719
Acid content: 0.33757 mol HCl per 1000 g. water.							
25.02	73.87	0	1.01930	0.33827	0.33831	0.33832	0.33831
25.02	74.23	1:00	1.01932	0.33830	0.33833	0.33834	0.33832
35.02	72.16	1:35	1.01931	0.33753	0.33756	0.33753	0.33752
35.01	72.19	2:55	1.01929	0.33752	0.33754	0.33752	0.33751
17.87	74.85	4:00	1.01930	0.33837	0.33840	0.33844	0.33842
17.89	74.82	4:35	1.01927	0.33848	0.33849	0.33853	0.33851
17.89	74.82	5:05	1.01929	0.33850	0.33851	0.33853	0.33852
Acid content: 0.10040 mol HCl per 1000 g. water.							
25.00	74.56	0	1.01995	0.39917	0.39919	0.39912	0.39911
17.86	75.42	8:00	1.01925	0.39781	0.39782	0.39774	0.39775
17.95	75.42	8:26	1.01928	0.39783	0.39787	0.39777	0.39778
18.05	75.42	8:52	1.01928	0.39787	0.39789	0.39777	0.39780
35.00	72.48	19:45	1.01961	0.39982	0.39990	0.39984	0.39986
35.15	72.48	20:25	1.01934	0.39981	0.39984	0.39979	0.39980
Acid content: 0.033315 mol HCl per 1000 g. water.							
25.04	74.25	0	1.01972	0.45265	0.45287	0.45283	0.45283
25.10	74.17	1:00	1.01930	0.45248	0.45270	0.45266	0.45267
35.00	72.36	2:50	1.01927	0.45507	0.45527	0.45520	0.45522
35.02	72.44	4:10	1.01929	0.45516	0.45535	0.45528	0.45530
17.81	75.19	7:10	1.01930	0.45018	0.45036	0.45036	0.45038
17.91	75.23	8:10	1.01926	0.45021	0.45038	0.45038	0.45040
Acid content: 0.01001 mol HCl per 1000 g. water.							
18.03	75.10	0	1.01930	0.52732	0.52731	0.52709	0.52742
18.06	75.21	1:05	1.01928	0.52743	0.52742	0.52717	0.52756
24.99	74.48	3:45	1.02038	0.53173	0.53182	0.53145	0.53242
24.99	74.47	9:15	1.01933	0.53034	0.53034	0.52985	0.53080
35.02	72.60	12:25	1.01933	0.53671	0.53681	0.53621	0.53746
35.02	72.58	13:30	1.01927	0.53664	0.53672	0.53613	0.53741
Acid content: 0.00333 mol HCl per 1000 g. water.							
25.00	74.24	0	1.01932	0.80798	0.81148	0.79777	0.79982
35.00	72.40	1:30	1.01935	0.81592	0.81594	0.80585	0.80439
35.00	72.40	2:25	1.01931	0.81596	0.81617	0.80577	0.80398

In Table V are summarized the final values of the electromotive force of the hydrogen-calomel cell for a hydrogen pressure of exactly one atmosphere, for temperatures of exactly 18, 25, or 35°, and at the indicated concentrations of hydrochloric acid. The values here given are the means for the four cells, the last made measurements being used in each case, and these being corrected as described at the beginning of this section. In this table and in the following ones values at small concentrations which are seriously affected by the unreliability of the calomel electrode referred to above (at the end of Section 3(b)) are enclosed within parentheses.

TABLE V.—SUMMARY OF THE ELECTROMOTIVE FORCES OF THE CELLS AND THEIR TEMPERATURE COEFFICIENTS.

Mols HCl in 1000 g. water.	Electromotive force.				
	At 18°.	At 25°.	At 35°.	10 ⁶ ₂₅ .	10 ⁶ ₂₅ .
4.484	0.15759	0.15506	0.15124	—2384	—7.82
1.9278	0.23769	0.23589	0.23304	—1137	—7.06
1.0381	0.27919	0.27802	0.27595	—663	—8.23
0.77137	0.29654	0.29571	0.29411	—460	—8.20
0.50948	0.31912	0.31865	0.31765	—253	—6.00
0.33757	0.33845	0.33836	0.33794	—75	—4.96
0.10040	0.39764	0.39884	0.40013	+386	—6.47
0.03332	0.45020	0.45258	0.45357	+715	—5.47
0.01001	(0.5271)	(0.5302)	(0.5369)	(+1010)	(+26.10)
0.003333	...	(0.8040)	(0.8105)

From these values of the electromotive force there have been derived equations expressing it as a temperature function for each concentration of acid. These equations are of the form

$$E_t = E_{25} [1 + \alpha_{25} (t - 25) + \beta_{25} (t - 25)^2].$$

The values of $10^6 \alpha_{25}$ and $10^6 \beta_{25}$ are given in the last two columns of Table V. These values of α give a good curve when plotted against the logarithm of the concentration, and are probably reliable; but the values of β exhibit only faint traces of regularity, owing to the fact that they are too small to be accurately determined.

5. Decrease in Free Energy and in Heat Content Attending the Cell Reaction.

Since on the passage of two faradays through the cell the change in state H_2 (1 atm.) + Hg_2Cl_2 (solid) = $2Hg$ (liquid) + $2HCl$ (at c) takes place, the free-energy decrease accompanying this reaction at any temperature and concentration is obtained by multiplying the corresponding electromotive force by 2×96500 .

If the free-energy decrease at any of these concentrations is expressed by a temperature function of the same form as that used for electromotive force, the temperature coefficients α_{25} and β_{25} will have the same values as they had in the electromotive force function.

Moreover, the decrease of heat content attending the change in state at 25° may be calculated from α_{25} , the temperature coefficient of the electromotive force, by the aid of the fundamental thermodynamic equation $d/dT (-\Delta F/T) = \Delta H/T^2$. On substituting in this equation the expression for $-\Delta F$ as a temperature function for any given concentration, performing the indicated differentiation, and rearranging the terms, there is obtained

$$-\Delta H_{25} = -\Delta F_{25} (1 - 298 \alpha_{25}).$$

Table VI contains the so calculated values of the free-energy decrease and also of the heat-content decrease in joules.

TABLE VI.—DECREASE IN FREE ENERGY AND IN HEAT CONTENT ATTENDING THE CELL REACTION.

Mols HCl per 1000 g. H ₂ O.	Free energy decrease.			Heat decrease. at 25°.
	At 18°.	At 25°.	At 35°.	
4.484	30415	29927	29190	51187
1.9278	45874	45527	44977	60952
1.0381	53884	53657	53257	64260
0.7714	57232	57072	56762	64896
0.5095	61590	61500	61307	66137
0.3376	65322	65303	65222	66766
0.10040	76745	76977	77224	68124
0.03332	86888	87348	87925	68734
0.01001	(101740)	(102330)	(103630)	(71530)
0.00333	..	(155170)	(156430)	...

The value of ΔH at 25° and 0.1 molal HCl calculated from the electromotive forces may be compared with that derived directly from thermochemical measurements. The heat of formation of 1 Hg₂Cl₂ is 62,600 cal. (Nernst¹), 62,640 cal. (Varet¹), 65,210 cal. (Thomsen¹), 62,900 (Koref²), 63,675 cal. (Wolff³), and 62,650 (Pollitzer⁴), the mean of these values, omitting Thomsen's, being 62,890 cal. The heat of formation of 1 HCl (gaseous) is 22,000 cal. according to Thomsen and Berthelot. The heat of solution of 1 HCl in 20 H₂O is according to Thomsen⁵ 16,760 cal. By plotting the values of the heat of dilution determined by Thomsen,⁵ Steinwehr,⁶ and Richards,⁷ it has been found that the heat of dilution of 1HCl.20H₂O to 1 HCl.555H₂O (where the HCl is 0.1 molal) is 590 cal.,⁸ making the heat of solution of 1 HCl in 555 H₂O 17,350 cal. From

¹ *Landolt-Börnstein Tabellen*, 4th Ed., p. 869.

² *Z. Electrochem.*, 18, 818 (1912).

³ *Ibid.*, 20, 19 (1914).

⁴ *Ibid.*, 19, 513 (1913).

⁵ *Landolt-Börnstein Tabellen*, 4th Ed., p. 885.

⁶ *Z. physik. Chem.*, 38, 185 (1903).

⁷ *THIS JOURNAL*, 32, 1776 (1910).

⁸ In order to enable this plot to be readily reconstructed, it may be stated that the heats of dilution of 1HCl.20H₂O corresponding to the curve best representing the re-

the plot, by drawing a tangent to the curve at the proper point, the heat of solution of 1 H₂O in an infinite amount of HCl.555H₂O was determined to be 0.104 cal., the corresponding value of the heat of solution of 555 H₂O being 58 cal. This gives for the heat of solution of 1 HCl in an infinite amount of HCl.555H₂O the value 17,290 cal.¹ From these values we get for the decrease in heat content attending the reaction $\text{H}_2 + \text{Hg}_2\text{Cl}_2 = 2\text{Hg} + 2\text{HCl}$ (at 0.1 molal) the value 15,690 cal. The value of the decrease in heat content derived from the electromotive force data and given in Table VI is 68,124 joules, corresponding to 16,290 cal. The agreement is probably as close as the accuracy of the thermochemical data permits.

6. Decrease in Free Energy and in Heat Content Attending the Transfer of Hydrochloric Acid from Any Concentration to 0.1000 Molal.

From the energy effects attending the reduction of calomel by hydrogen with formation of hydrochloric acid at various concentrations we can, by simple subtraction, obtain the energy effects attending the transfer of hydrochloric acid from a solution of one concentration into one of another concentration. It seems best to adopt 0.1000 molal as the concentration of reference, as this is the smallest concentration at which the electromotive forces are apparently still entirely free from error. The decreases in free energy and in heat content attending the cell reaction have therefore been first calculated for this round concentration from empirical equations expressing the electromotive forces at the three neighboring concentrations, 0.3376, 0.10040, and 0.03332 molal, at each of the three temperatures. In this way the following values (in volts and joules) for the cell reaction at the concentration 0.1000 were obtained.

Temperature.	18°.	25°.	35°.
Electromotive force.....	0.39783	0.39904	0.40033
Free-energy decrease.....	76782	77015	77263
Heat-content decrease.....	...	68134	...

By subtracting from these values of the free-energy decrease and heat-content decrease those given in Table VI and dividing by 2, values for the free energy of transfer and heat of transfer of 1 HCl from any concentrations of the three investigators were as follows: to 1HCl.30H₂O, 192 cal.; to 1HCl.50H₂O, 336 cal.; to 1HCl.100H₂O, 445 cal.; to 1HCl.200H₂O, 515 cal.; to 1HCl.400H₂O, 564 cal.; to 1HCl.800H₂O, 605 cal.; to 1HCl.2000H₂O, 646 cal.

¹ This follows from the relation $\frac{\partial Q}{\partial N_A} + 555 \frac{\partial Q}{\partial N_W} = Q_0^{555}$ in which the partial derivatives represent the "partial" heats of solution of one mol of the acid (A) and water (W), respectively, and Q_0^{555} represents the heat of solution of 1 HCl in 555 H₂O. This relation follows from the fact that the solution 1HCl.555H₂O may be produced either by mixing directly the two constituents 1 HCl and 555 H₂O or by introducing them in succession into an infinite quantity of solution of this composition.

tion to the concentration 0.1000 molal were obtained. These values expressed in joules are given in Table VII.

TABLE VII.—DECREASE IN FREE ENERGY AND IN HEAT CONTENT ATTENDING THE TRANSFER OF 1 HCl FROM ANY CONCENTRATION TO 0.1000 MOLAL.

Conc. HCl.	$-\Delta F_{15}$	$-\Delta F_{25}$	$-\Delta F_{35}$	$-\Delta H_{25}$	10 ⁶ s.	10 ⁶ h.
4.484	23184	23544	24037	8474	2149	5.5
1.9278	15454	15744	16143	3591	2591	5.5
1.0381	11449	11679	12003	1937	2790	2.2
0.77137	9775	9971	10250	1619	2811	1.3
0.50948	7596	7757	7978	999	2924	8.0
0.33757	5730	5856	6021	684	2963	15.0
0.10000	0	0	0	0
0.033315	-5053 ¹	-5167 ¹	-5331 ¹	-300	3161	7.3
0.01001	(-12477)	(-12657)	(-13183)	(-1700)	(2904)	..

The variation of the free energy of transfer with the temperature may be expressed for each concentration of acid by equations of the form

$$(-\Delta F_t)_c = (-\Delta F_{25})_c [1 + a(t - 25) + b(t - 25)^2];$$

where $(-\Delta F_{25})_c$ means the free-energy decrease attending the transfer of 1 HCl at 25° from concentration c to concentration 0.1000 molal. The values of these coefficients a and b (multiplied by 10⁶) are given in the last two columns of Table VII.

The values of a just given would be equal to $1/T$ or 0.00335, if the change in heat content accompanying the transfer of 1 HCl from one concentration to another were zero, as would be the case if the hydrochloric acid were a perfect solute. The values of a approach this theoretical value as the acid concentration decreases, but they are still far from it even for the two lower concentration intervals 0.3376 to 0.1000 and 0.1000 to 0.03332. Correspondingly the values of the change in heat content are still large for these two concentration intervals.

These heats of transfer may be compared with values of the same quantity computed from the calorimetric measurements made by Thomsen, Steinwehr, and Richards mentioned near the end of Section 5. From the curve there referred to were read off values of the heat change on adding a definite amount of water to a definite amount of HCl solution of a given concentration. From tangents drawn to the curve the heat changes on adding 1 mol H₂O to an infinite amount of various HCl solutions (the so-called partial heat of solution of water) were obtained. From these two quantities the heats of transfer of 1 HCl into a solution containing 1 HCl in 10 liters of water from solutions containing 1 HCl in 0.494 liter, 1.30 liters, and 2.965 liters of water were calculated to be 990, 279, and 117 calories, respectively. The electromotive forces of this article lead

¹ It seems not improbable that these values are about 130 joules too large (arithmetically), judging from the magnitude of the error at the two lowest concentrations.

to the values 859, 387, and 164 calories for the same heats of transfer. The agreement is probably as good as can be expected from the data.

7. Relative Activities of the Ions of the Acid at Various Concentrations.

From the values for the free energy of transfer of hydrochloric acid the relative activities of the hydrogen ion and chloride ion in different solutions may be calculated by the equation $-\Delta F = 2 R T \log (c_1 \alpha_1 / c_2 \alpha_2)$. In this equation $-\Delta F$ is the free energy of transfer of 1 HCl from concentration c_1 to concentration c_2 , and the symbols α_1 and α_2 represent the coefficients by which it is necessary to multiply the concentration of the acid in any solution in order to obtain the activity of the hydrogen ion or chloride ion in the solution. This quantity α will be called the activity coefficient. This equation involves the assumption that the activity of the hydrogen ion is equal to that of the chloride ion in each of the hydrochloric acid solutions. If this assumption is not valid, the calculated values of α represent the square root of the product of the activities of the two ions.

The values calculated by this equation for the ratio $(\alpha/\alpha_{0.1})$ of the activity coefficient of the acid at any concentration c to that at the concentration 0.1000 molal at 18, 25, and 35° are given in Table VIII.

TABLE VIII.—RELATIVE ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID.
Activity coefficient ratios $(\alpha/\alpha_{0.1})$.

Mols HCl per 1000 g. H ₂ O.	Activity coefficient ratios $(\alpha/\alpha_{0.1})$.		
	At 18°.	At 25°.	At 35°.
4.484	2.647	2.571	2.424
1.928	1.260	1.241	1.209
1.038	1.024	1.017	1.001
0.7714	0.975	0.970	0.957
0.5095	0.942	0.939	0.931
0.3376	0.967	0.966	0.959
0.10000	1.000	1.000	1.000
0.03332	1.057	1.058	1.061
0.01001	...	(0.779)	...
0.003333	...	(0.0113)	...

8. Combination of the Free Energy Values with those Derivable from Other Electromotive-Force Measurements.

The results here presented can not be compared with those of Jahn or of Tolman and Ferguson because their measurements relate to a range of concentrations below 0.1 molal. By combining, however, my results with the apparently very accurate ones of Jahn a series of free energy values for hydrochloric acid in solution can be obtained extending from 0.00167 to 4.48 molal. The free-energy decrease in joules attending the transfer of 1 HCl at 18° from 0.03336 molal (the highest concentration used by Jahn) to various lower concentrations c have been calculated by me from the electromotive forces and the cation transference number (0.826) given by Jahn. By adding to these values 5039 joules (which

is equal to the quantity (5053 joules) given in Table VII for the transfer from 0.1000 to 0.03332 molal plus the quantity, —14 joules, calculated for the transfer from 0.03332 to 0.03342 molal), the free energy of transfer of 1 HCl at 18° from 0.1000 molal to various lower concentrations is obtained.

The values so found are given, expressed in joules, in Table IX. The concentrations have been calculated over from the volume concentrations used by Jahn to mols HCl per 1000 g. water.

TABLE IX.—THE FREE ENERGY ATTENDING THE TRANSFER AT 18° OF 1 HCl FROM 0.1000 MOLAL TO VARIOUS SMALL CONCENTRATIONS.

Mols HCl per 1000 g. H ₂ O.	Free-energy decrease.	Mols HCl per 1000 g. H ₂ O.	Free-energy decrease.
0.03342	5039	0.006683	12472
0.01668	8224	0.005569	13325
0.01115	10084	0.003334	15717
0.00832	11447	0.001667	19031

By combining the values of the free-energy decrease attending the cell reaction given in Table VI with the free-energy decrease attending the reaction $2\text{Hg} + \text{Cl}_2$ (1 atm.) = Hg_2Cl_2 (solid) one may obtain the free energy of 1 HCl (referred to its elements) in solution at the various concentrations and temperatures. Now Lewis and Rupert¹ found the electromotive force of the cell $\text{Hg} + \text{Hg}_2\text{Cl}_2, \text{HCl}$ (0.1 M.), Cl_2 (1 atm.) to be 1.0896 volts at 25°. The free energy of formation of 1 Hg_2Cl_2 at 25° is therefore —50,250 cal. With the aid of its heat of formation (—62,890 cal.) its free energy of formation is found to be —50,510 cal. at 18° and —49,860 cal. at 35°.

Table X contains the values calculated in this manner for the free energy in calories of 1 HCl in solution, the free energies of its elements being regarded as zero at each temperature.

TABLE X.—FREE ENERGY OF 1 HCl IN SOLUTION AT VARIOUS CONCENTRATIONS AND TEMPERATURES.

Mols HCl per 1000 g. H ₂ O.	Free energy in calories.			Mols HCl per 1000 g. H ₂ O.	Free energy at 18°.
	At 18°.	At 25°.	At 35°.		
4.484	—28890	—28700	—28410	0.01668	—36410
1.9278	—30750	—30570	—30300	0.01115	—36850
1.0381	—31700	—31540	—31290	0.008324	—37180
0.7714	—32100	—31950	—31710	0.006683	—37420
0.5095	—32620	—32480	—32250	0.005569	—37630
0.3376	—33070	—32930	—32720	0.003334	—38200
0.1000	—34440	—34330	—34160	0.001667	—38990
0.03332	—35650	—35570	—35440		

This table might be extended so as to include more concentrated solutions with the aid of Dolezalek's² measurements of the electromotive

¹ THIS JOURNAL, 33, 305 (1911).

² Z. physik. Chem., 26, 334 (1898).

force of cells H_2 , HCl (4.98 to 12.25 normal), Cl_2 . However, as his measurements were at 30° and as his electromotive forces were not reproducible closer than 6 millivolts, this reference to them will be sufficient.

By combining these free energies with vapor-pressure data it would be possible to obtain also the free-energy content of hydrogen chloride gas at any pressure. Such data have been obtained by Gahl¹ at the acid concentrations involved in this investigation; but calculation shows that Gahl's results do not agree well with the electromotive-force data above presented. He gives 0.0094 and 0.00117 mm. mercury as the partial pressures at 25° of HCl in the solutions containing 4.007 and 2.011 mols HCl per 1000 g. water. From these vapor pressures the free energy of transfer of HCl from 4.007 molal to 2.011 molal is found by the equation $-\Delta F = R T \log (940/117)$ to be 5170 joules. Interpolation from the electromotive-force measurements gives 6280 joules for the same free-energy decrease. Since Gahl's results at higher concentrations are also discordant with those of Dolezalek,² it is doubtful whether they are accurate enough to warrant the calculation of the free energy of gaseous hydrogen chloride from them.

9. Discussion of the Activity Coefficients of Hydrochloric Acid and Potassium Chloride.

From the free-energy values derived from Jahn's measurements we can calculate in the same way as was done above the relative activity coefficients of the acid at various concentrations; and, by combining these with the activity coefficients presented in Table VIII, a series of relative activity coefficients extending from 0.00167 to 4.484 molal is obtained. Assuming provisionally that at this lowest concentration the activity coefficient is substantially equal to the so-called ionization-coefficient derived from the conductance ratio, a series of absolute activity coefficients may be calculated. This assumption, to be sure, probably introduces a considerable error; for Jahn's data indicate that the activity coefficient continues to increase more rapidly than the conductance ratio even below the concentration 0.00167, which would make all the activity coefficients considerably smaller than those calculated. Any attempt to extrapolate would, however, be so arbitrary that it has not been attempted at this time, and the stated assumption has been employed provisionally.

The values of the activity coefficients at 18° so calculated and interpolated for round concentrations are given in Table XI. In this table in a neighboring column are given also, for the sake of comparison, values of the conductance-viscosity ratio $\Delta\eta/\Delta_o\eta_o$ at the same concentrations.

¹ *Z. physik. Chem.*, 33, 178 (1900).

² *Ibid.*, 26, 334 (1898).

The values employed up to 0.2 molal are those of Bray and Hunt¹ as corrected for viscosity by Noyes and Falk,² and those at the concentrations 0.5 and 1.0 molal are based on the data of Kohlrausch³ and the viscosity determinations of Reyher.⁴

TABLE XI.—ACTIVITY COEFFICIENTS AND CONDUCTANCE VISCOSITY RATIOS FOR HYDROCHLORIC ACID AT 18°.

Mols HCl per 1000 g. H ₂ O.	Activity coefficient.	$A\eta/A_0\eta_0$.	Mols HCl per 1000 g. H ₂ O.	Activity coefficient.	$A\eta/A_0\eta_0$.
0.001677	0.988	0.988	0.20	0.818	0.909
0.002	0.987	0.988	0.30	0.804	0.903
0.005	0.971	0.981	0.50	0.793	0.890
0.010	0.947	0.972	0.75	0.820	0.870
0.020	0.918	0.962	1.00	0.857	0.845
0.050	0.874	0.944	2.00	1.086	...
0.100	0.843	0.925	4.484	2.228	...

It will be seen that with increasing concentration the activity coefficient first falls much more rapidly than the conductance-viscosity ratio, the two values at 0.1 molal being 0.843 and 0.925. The activity coefficient, however, unlike the conductance-viscosity ratio, passes through a minimum at about 0.50 molal, and then increases rapidly with the concentration, becoming about equal to that ratio at 1 molal, and attaining at 4.48 molal a value 2.23 times as great as that at zero concentration.

It is of interest to compare the activity coefficients of hydrochloric acid with those of potassium chloride at 25° derived from the accurate electromotive-force measurements of MacInnes and Parker.⁵ The reliability of their results is evidenced by the fact that their two series of measurements made with cells of the two types $\text{Ag} + \text{AgCl}, \text{KCl}(c_1)$, $\text{KCl}(c_2)$, $\text{AgCl} + \text{Ag}$, and $\text{Ag} + \text{AgCl}, \text{KCl}(c_1)$, $\text{K}_\text{m}\text{Hg}, \text{KCl}(c_2)$, $\text{Ag} + \text{AgCl}$ gave closely concordant results, and that their results agree well with those obtained by Jahn at 18°. The electromotive force values obtained by MacInnes and Parker have, for the sake of comparison, been treated in the same way as have those obtained in this investigation. Namely, the free-energy decrease attending the transfer of 1 HCl from concentration c_1 to concentration c_2 was calculated from them, using as the cation-transference number⁶ 0.497 for concentrations up to 0.1 normal and 0.495 for the concentration-interval 0.05–0.5. Then the corresponding activity-coefficient was calculated from them by the usual logarithmic formula, making the same provisional assumption as MacInnes and Parker made in their own calculations of the activity coefficients, namely,

¹ THIS JOURNAL, 33, 787 (1911).

² *Ibid.*, 34, 475 (1912).

³ *Landolt-Börnstein Tabellen*, 4th Ed., p. 1104.

⁴ *Z. physik. Chem.*, 2, 744 (1888).

⁵ THIS JOURNAL, 37, 1445–1461 (1915).

⁶ Noyes and Falk, *Ibid.*, 34, 474 (1912).

that the activity coefficient and conductance ratio are identical at 0.001 molal, the smallest concentration employed.

The results are presented in Table XII. The type of cell by means of which they were derived is indicated by the letters A and B, A referring to the simple concentration cell with silver-silverchloride electrodes, and B to the double cell with amalgam electrodes.

TABLE XII.—FREE ENERGY OF TRANSFER OF POTASSIUM CHLORIDE AND ITS ACTIVITY COEFFICIENTS.

Concentration.		Type of cell.	Free-energy decrease.	Activity coefficient at α .	Conductance ratio at α .
α .	α .				
0.50	0.05	A	10360	0.636	0.779
		B	10440		
0.10	0.01	A	10510	0.727	0.860
		B	10485		
0.05	0.005	A	10700	0.781	0.889
		B	10630		
0.01	0.001	B	10870	0.876	0.941
0.005				0.911	0.956
0.001				(0.979)	0.979

MacInnes and Parker have already drawn from their data the more essential conclusions; but this table, especially when considered in connection with Tables IX and XI for hydrochloric acid, brings out clearly certain relations. In the first place it shows the close agreement of the results obtained by MacInnes and Parker with the two types of cells. Then it shows that even for the lowest ten-fold concentration interval the free-energy decrease (10,870 for KCl, 10,810 for HCl) is still far from the value (11,420 joules) for a completely ionized perfect solute, and that correspondingly the activity coefficient still changes considerably during that interval, namely, by over 10% for both substances. It shows further that with potassium chloride, as with hydrochloric acid, the activity coefficient up to 0.1 normal decreases much more rapidly than the conductance ratio, being at this concentration 15% lower for potassium chloride and 9% lower for hydrochloric acid. It shows finally that the activity coefficient at corresponding concentrations is many per cent. smaller for potassium chloride than for hydrochloric acid, thus disproving the assumption sometimes made that the activity coefficients of these two substances can be regarded as equal.

Finally, a comparison may be made between the values of the activity coefficients of potassium chloride derived from the electromotive-force measurements and those derived from freezing-point determinations by the method recently described by Bates.¹ With the aid of the laws of thermodynamics and of the two assumptions that the two ions in the same solutions have equal osmotic pressures and that the true value

¹ THIS JOURNAL, 37, 1421-1445 (1915).

of the ionization is given by the conductance-viscosity ratio, he found that the change at 0° of the osmotic pressure π of either ion with its concentration $c\gamma$ is expressed in the case of potassium chloride by the equation $d\pi/d(c\gamma) = RT (1 - 0.0552(c\gamma)^{0.207})$. From this equation and the two thermodynamic relations

$$-\Delta F = \int_{\pi_2}^{\pi_1} \frac{d\pi}{c\gamma} \text{ and } -\Delta F = RT \log \frac{c_1 \alpha_1}{c_2 \alpha_2},$$

supplemented by the assumption that the activity coefficient α approaches unity as the salt concentration c approaches zero, the activity coefficients corresponding to Bates' osmotic pressure calculations are found to have the values given in the second line of Table XIII while those derived from the electromotive-force measurements of MacInnes and Parker were shown in Table XII to have the values recorded in the third line of Table XIII.

TABLE XIII.—COMPARISON OF THE ACTIVITY COEFFICIENTS OF POTASSIUM CHLORIDE DERIVED FROM FREEZING-POINT AND FROM ELECTROMOTIVE-FORCE MEASUREMENTS.

Salt concentration.....	0.01	0.05	0.10	0.50
Activity coefficient (Bates).....	0.884	0.772	0.732	0.640
Activity coefficient (M. & P.).....	0.876	0.781	0.727	0.636

The close agreement throughout the whole range of concentration of the two sets of activity values based upon entirely independent experimental data is highly remarkable. If confirmed by results with other substances it will afford proof of the hypothesis that the conductance viscosity ratio is a substantially correct measure of ion concentration (though not of ion activity); for, as stated above, Bates' calculations involve this assumption, while the calculations from the electromotive forces are independent of it. Unfortunately, sufficiently accurate freezing-point data are not available for hydrochloric acid to enable corresponding computations to be made in the case of this substance.

10. Summary.

In this article the preparation of calomel electrodes reproducible to 0.05 millivolt when in contact with hydrochloric acid 0.1 molal or higher has been described; and measurements of the electromotive force of cells of the type H_2 (1 atm.), HCl solution, $Hg_2Cl_2 + Hg$ at 18° , 25° , and 35° , and with HCl concentrations from 0.033 to 4.5 molal have been presented (Table V).

From these electromotive-force values have been computed:

1. The change in free-energy content and in heat content attending the reaction H_2 (1 atm.) + Hg_2Cl_2 (solid) = $2Hg$ (liquid) + $2HCl$ at various concentrations (Table VI).
2. The change in free-energy content and in heat content attending the change HCl (at c_1) = HCl (at c_2) (Table VII).
3. The ratio of the activities of the hydrogen ion or chloride ion in solutions of various concentrations (Table VIII).

By combining these results with those derived from Jahn's measurements of the electromotive force at 18° of cells $\text{Ag} + \text{AgCl}, \text{HCl}(c_1), \text{HCl}(c_2), \text{AgCl} + \text{Ag}$ the series of free-energy values has been extended from 0.033 to 0.00167 molal (Table IX). And with the aid of calorimetric data and an electromotive force determination of the cell $\text{H}_2, \text{HCl}, \text{Hg}_2\text{Cl}_2 + \text{Hg}$ by Lewis and Rupert, the absolute free energy of HCl (referred to the free energies of the elements as zero) at 18, 25, and 35° in solutions from 0.00167 molal to 4.5 molal has been calculated and tabulated (Table X).

From these free-energy data, with the aid of the assumption that at the lowest concentration (0.00167 molal) the ion activity is equal to the ion concentration, a series of absolute activity coefficients for hydrochloric acid covering the concentration range 0.00167–4.5 molal has been computed (Table XI). These have then been compared with the activity coefficients of potassium chloride derived from the electromotive-force measurements of MacInnes and Parker (Table XII) and the osmotic pressure calculations of Bates (Table XIII).

The results lead to the conclusions that the activity coefficients both of hydrochloric acid and potassium chloride decrease up to 0.1 molal far more rapidly than do the conductance ratios. The difference at this concentration amounts to 9% for hydrochloric acid and 15% for potassium chloride, so that in using the conductance ratio as a measure of ion activity in mass-action expressions, as is commonly done, a corresponding error is involved. At a concentration of about 0.5 molal the activity coefficient of hydrochloric acid reaches a minimum, and then increases very rapidly with increasing concentration, becoming at the highest concentration (4.48 molal) 2.23 times as great as at zero concentration. The results show further that the activity coefficients of potassium chloride derived independently from electromotive force and from freezing-point measurements are in remarkable agreement, affording evidence that in the case of this salt the conductance ratio is a true measure of ion concentration (though not of ion activity), since this assumption is made in the calculation from the freezing points, but not in that from the electromotive forces.

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THE ATOM AND THE MOLECULE.

By GILBERT N. LEWIS.

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In a paper entitled "Valence and Tautomerism"¹ I took occasion

¹ THIS JOURNAL, 35, 1448 (1913); see also the important article of Bray and Branch, *Ibid.*, 35, 1440 (1913).

to point out the great importance of substituting for the conventional classification of chemical substances, as inorganic or organic, the more general classification which distinguishes between polar and nonpolar substances. The two classifications roughly coincide, since most inorganic substances are distinctly polar, while the majority of organic substances belong to the nonpolar class; thus potassium chloride represents the extreme polar type and methane the nonpolar. Nevertheless, there are many inorganic substances which, under ordinary circumstances, are predominantly nonpolar, and many organic substances which, at least in a certain part of the molecule, are strongly polar.

This article was apparently unknown to Sir. J. J. Thomson¹ when he wrote, in 1914, an extremely interesting paper on the "Forces between Atoms and Chemical Affinity" in which he reached conclusions in striking accord with my own, and discussed in considerable detail the theories of atomic and molecular structure which led him to these conclusions.

To enable us to appreciate the importance and the usefulness of a distinction between the polar and nonpolar types of chemical molecules no hypotheses are necessary, but in a more minute examination of the nature of such a distinction some theory of atomic structure is indispensable. Such a theory I have employed for a number of years in the interpretation of chemical phenomena, but it has not hitherto been published. I shall present this theory briefly in the present paper, for, while it bears much resemblance to some current theories of the atom, it shows some radical points of departure from them. As an introduction it will be desirable to review the characteristics of polar and nonpolar compounds.

Polar and Nonpolar Types.

The very striking differences in properties between the extreme polar and the extreme nonpolar types are summarized in the following table quoted from my previous paper:

POLAR.	NONPOLAR.
Mobile	Immobile
Reactive ²	Inert
Condensed structure	Frame structure
Tautomerism	Isomerism
Electrophiles	Non-electrophiles
Ionized	Not ionized
Ionizing solvents	Not ionizing solvents
High dielectric constant	Low dielectric constant
Molecular complexes	No molecular complexes
Association	No association
Abnormal liquids	Normal liquids

¹ *Phil. Mag.*, 27, 757 (1914).

² In my former paper the words "inert" and "reactive" were inadvertently transposed and appear in the wrong columns.

All of these properties with respect to which fundamental distinctions have been made between the two types, and which seem so unconnected, are in fact closely related, and the differences are all due to a single cause. Even before making any more special hypothesis we may very safely assume that the essential difference between the polar and the nonpolar molecule is that, in the former, one or more electrons are held by sufficiently weak constraints so that they may become separated from their former positions in the atom, and in the extreme case pass altogether to another atom, thus producing in the molecule a bipole or multipole of high electrical moment. Thus in an extremely polar molecule, such as that of sodium chloride, it is probable that at least in the great majority of molecules the chlorine atom has acquired a unit negative charge and therefore the sodium atom a unit positive charge, and that the process of ionization consists only in a further separation of these charged parts.

If then we consider the nonpolar molecule as one in which the electrons belonging to the individual atom are held by such constraints that they do not move far from their normal positions, while in the polar molecule the electrons, being more mobile, so move as to separate the molecule into positive and negative parts, then all the distinguishing properties of the two types of compounds become necessary consequences of this assumption, as we may readily show.

Thus polar compounds with their mobile parts fall readily into those combinations which represent the very few stable states, while the nonpolar molecules, in which the parts are held by firmer constraints, are inert and unreactive, and can therefore be built up into the numerous complicated structures of organic chemistry. Many organic compounds, especially those containing elements like oxygen and nitrogen, and those which are said to be unsaturated, show at least in some part of the molecule a decidedly polar character. In such cases we have the phenomenon of tautomerism, where two or more forms of the molecule pass readily into one another and exist together in a condition of mobile equilibrium. Tautomerism is not characteristic of organic substances, but is, on the other hand, a predominant trait of most inorganic substances, which behave as if a great variety of forms were existing together in extremely mobile equilibrium.

When a molecule owing to the displacement of an electron, or electrons, becomes a bipole (or multipole) of high electrical moment, that is, when its charged parts are separated by an appreciable distance, its force of attraction for another molecular bipole will be felt over a considerable intervening distance, and two or more such bipoles will frequently be drawn together into a single aggregate in which the positive part of one molecule is brought as near as possible to the negative part of another. The molecules of a polar substance will therefore not only exhibit an

unusually high intermolecular attraction at a distance, but will frequently combine with one another and show the phenomenon known as association. It is indeed the substances which are distinctly polar, like ammonia, water, acids, and alcohols, which constitute, on account of association as well as of high intermolecular attraction, a class of liquids which are called abnormal with respect to numerous properties such as critical point, vapor pressure, heat of vaporization, viscosity, and surface tension.

Moreover a polar substance will combine with other substances to form those aggregates which are sometimes known as molecular compounds or complexes, and it may so combine with substances which are not of themselves markedly polar, for in the presence of a polar substance all other substances become more polar.

This important effect of polar molecules in rendering others more polar, to which I called attention in my previous paper, has been discussed in some detail by Thomson. A molecular bipole of small molecular moment, which would scarcely attract a similar molecule, will be very appreciably attracted by a polar molecule or bipole of high moment, and may form with it a double molecule. In this process the weaker bipole stretches and its moment increases. In general, if two molecules combine, or even approach one another, each weakens the constraints which hold together the charge of the other, and the electrical moment of each is increased.

This increase in the polar character of a molecule when combined with, or in the neighborhood of, other polar molecules is to a remarkable degree cumulative, for when two molecules by their approach or combination become more polar they draw other molecules more strongly towards them, but this still further increases their polar character. This is strikingly illustrated in numerous phenomena. Thus two substances in the gaseous state may differ but little in polar character, but when they are condensed to liquids the differences are frequently enormous.

The polar character of a substance depends, therefore, not only upon the specific properties of the individual molecules, but also upon what we may call the strength of the polar environment. Without attempting to give any quantitative definition of our terms we may plot, as in Fig. 1, the degree of polarity of a substance as ordinate and the strength of the polar environment as abscissa.

We then have for all substances a curve of the type shown in the figure where the dotted line represents the highest degree of polarity, namely complete ionization. Different pure substances in

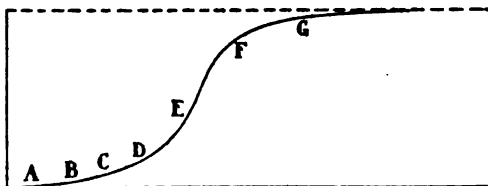


Fig. 1.

the liquid state come at different points, thus, roughly, hexane at A; benzene at B; ether at C; esters at D; water, ammonia, alcohols, amines, acids between D and F; and fused salts at G. In the last case, since the substance has nearly reached its highest possible polarity, it will not be much affected by an increase in the strength of the polar environment. At the other end of the curve a substance at A in a strong polar environment may move to B, and one at B may move to C, but they would not become markedly polar. It is in the intermediate range that substances are most affected by small changes in the environment. Thus hydrochloric acid, which in the pure state is not extremely polar, reaches nearly the highest possible state of polarity when dissolved in water. Such a change in this region is often much accentuated by the formation of complexes, and thus we have the rule of Abegg and Bodländer that a weak electrolyte usually becomes a strong electrolyte when its weak ion is converted into a complex ion.

We come then to the consideration of the electrical properties which distinguish polar from nonpolar substances, or, in accordance with the terminology which I formerly used,¹ which distinguish good electrophiles from poor electrophiles.

The first difference is in the dielectric constant. The difference between the dielectric constant of a substance and that of free space measures directly the number of free charges in the substance multiplied by the average distance through which these charges move under the influence of a definite electric field. In the polar molecule the constraints which operate against a separation of the charges, being already weak, may be further stretched in the electric field, and what is more important, the bi-poles (or multipoles) which already exist in the polar substance may, by rotation, orient themselves in the electric field, thus producing a large displacement current and therefore a high dielectric constant. In this connection Thomson has called attention to the work of Baedeker,² which shows that even in the gaseous state such substances as ammonia, water and hydrochloric acid possess an abnormally high dielectric constant.

Finally the polar substance, whether in the pure state or dissolved in another solvent, will obviously be the one which will be readily ionized. Moreover, polar substances are the strong ionizing solvents, for when another substance is combined with a highly polar substance, or even dissolved in such a solvent without actual combination of molecules, the degree of its own polarity largely increases.

Wide apart as the polar and nonpolar types are in the extreme, we must nevertheless inquire whether the difference is one of kind or one of degree.

¹ Lewis and Wheeler, *Z. physik. Chem.*, 56, 189 (1906).

² *Z. physik. Chem.*, 36, 305 (1901).

If there were a sharp and always recognizable distinction between the polar and the nonpolar molecule then a substance would be more polar or less polar according as it possessed a greater or smaller percentage of molecules of the first type. This would be a simple and in many cases a satisfactory interpretation of the difference in behavior between different substances, but scanning the whole field of chemical phenomena we are, I believe, forced to the conclusion that the distinction between the most extreme polar and nonpolar types is only one of degree, and that a single molecule, or even a part of a molecule, may pass from one extreme type to another, not by a sudden and discontinuous change, but by imperceptible gradations. The nature of such a transition we shall discuss in the following sections:

The Cubical Atom.

A number of years ago, to account for the striking fact which has become known as Abegg's law of valence and countervalence, and according to which the total difference between the maximum negative and positive valences or polar numbers of an element is frequently eight and is in no case more than eight, I designed what may be called the theory of the cubical atom. This theory, while it has become familiar to a number of my colleagues, has never been published, partly because it was in many respects incomplete. Although many of these elements of incompleteness remain, and although the theory lacks to-day much of the novelty which it originally possessed, it seems to me more probable intrinsically than some of the other theories of atomic structure which have been proposed, and I cannot discuss more fully the nature of the differences between polar and nonpolar compounds without a brief discussion of this theory.

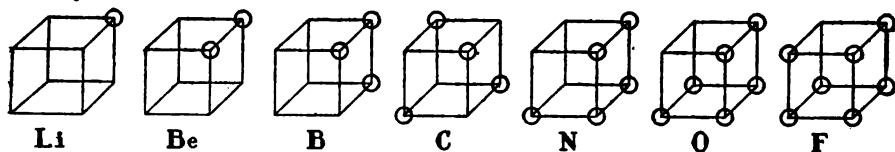


Fig. 2.

The pictures of atomic structure which are reproduced in Fig. 2,¹ and in which the circles represent the electrons in the outer shell of the

¹ These figures are taken from a memorandum dated March 28, 1902, together with the models are notes concerning different types of chemical compounds; the various possible arrangements of electrons in the outer atom and the possibility of intra-atomic isomerism; the relationship between symmetrical structure and atomic volume; and certain speculations as to the structure of the helium atom which we shall see were probably partly incorrect. The date of origin of this theory is mentioned not with the purpose of claiming any sort of priority with respect to those portions which overlap existing theories, but because the fact that similar theories have been developed independently adds to the probability that all possess some characteristics of fundamental reality.

neutral atom, were designed to explain a number of important laws of chemical behavior with the aid of the following postulates:

1. In every atom is an essential *kernel* which remains unaltered in all ordinary chemical changes and which possesses an excess of positive charges corresponding in number to the ordinal number of the group in the periodic table to which the element belongs.

2. The atom is composed of the kernel and an *outer atom* or *shell*, which, in the case of the neutral atom, contains negative electrons equal in number to the excess of positive charges of the kernel, but the number of electrons in the shell may vary during chemical change between 0 and 8.

3. The atom tends to hold an even number of electrons in the shell, and especially to hold eight electrons which are normally arranged symmetrically at the eight corners of a cube.¹

4. Two atomic shells are mutually interpenetrable.

5. Electrons may ordinarily pass with readiness from one position in the outer shell to another. Nevertheless they are held in position by more or less rigid constraints, and these positions and the magnitude of the constraints are determined by the nature of the atom and of such other atoms as are combined with it.

6. Electric forces between particles which are very close together do not obey the simple law of inverse squares which holds at greater distances.

Some further discussion of these postulates is necessary in order to make their meaning clear. The first postulate deals with the two parts of the atom which correspond roughly with the inner and outer rings of the Thomson atom. The kernel being that part of the atom which is unaltered by ordinary chemical change is of sufficient importance to merit a separate symbol. I propose that the common symbol of the element printed in a different type be used to represent the kernel. Thus Li will stand for the lithium kernel. It has a single positive charge and is equivalent to pure lithium ion Li^+ . Be has two positive charges, B three, C four, N five, O six and F seven.

We might expect the next element in the series, neon, to have an atomic kernel with eight positive charges and an outer shell consisting of eight electrons. In a certain sense this is doubtless the case. However, as has been stated in Postulate 3, a group of eight electrons in the shell is extremely stable, and this stability is the greater the smaller the difference in charge between the nucleus and this group of eight electrons. Thus in fluoride ion the kernel has a charge of $+7$, and the negative charge of the group of eight electrons only exceeds it by one unit. In fact in compounds of fluorine with all other elements, fluorine is assigned the polar number -1 . In the case of oxygen, where the group of eight

¹ We shall see later the advisability of modifying this assumption of the cubic arrangement of the fundamental group of eight electrons.

electrons has a charge exceeding that of the kernel by two units, the polar number is considered to be -2 in nearly every compound. Nitrogen is commonly assumed to have the polar number -3 in such compounds as ammonia and the nitrides. It may be convenient to assign occasionally to carbon the polar number -4 , but it has never been found necessary to give boron a polar number -5 , or beryllium -6 , or lithium -7 . But neon, with an inner positive charge of 8 and an outer group of eight electrons, is so extremely stable that it may, as a whole, be regarded as the kernel of neon and we may write $\text{Ne} = \text{Ne}^1$.

The next element, sodium, begins a new outer shell² and $\text{Na} = \text{Na}^+$, $\text{Mg} = \text{Mg}^{++}$, and so on. In my original theory I considered the elements in the periodic table thus built up, as if block by block, forming concentric cubes. Thus potassium would be like sodium except that it would have one more cube in the kernel. This idea, as we shall see, will have to be modified, but nevertheless it gives a concrete picture to illustrate the theory.

We have then as kernels³ with a single positive charge H, Li, Na, K, Rb, Cs; with two positive charges Be, Mg, Ca, Sr, Ba; with three charges B, Al, Sc; with four charges C, Si; with five charges N, P, As, Sb, Bi; with six charges O, S, Se, Te and a group of radioactive isotopes; with seven charges F, Cl, Br, I; and with zero charge He, Ne, A, Kr, Xe and Nt. These elements only will be discussed in the present paper. The remaining elements form a class in which the atomic kernel is probably neither uniquely determined nor invariable during chemical change. This is one of the elements of incompleteness in the theory. Nevertheless this classification is not arbitrary but is forced upon us, and the elements which are included furnish so large a part of the material upon which the science of chemistry is based, that the study of their compounds offers in itself a problem of great importance.

Postulate 2 cannot be fully discussed except in connection with the fourth postulate, but assuming that we understand the meaning of the reduction or oxidation of an element (at least in the case of highly polar

¹ It must not be assumed, even in the case of the elements here chosen for discussion, that the distinction between kernel and shell is absolutely hard and fast. Thus in the ionization of neon by electric discharge, electrons must be thrown off from the group which we consider as belonging to the kernel itself.

² The periodicity in the table of elements, due to successive additions of groups of eight electrons to the atomic kernel, is imitated closely by compounds. Thus ammonium ion has nine positive charges in the kernels and eight electrons in the shells, but these eight electrons forming a stable group make ammonium ion entirely analogous to the kernel of an alkali metal.

³ I believe that it will be easily remembered that the sodium kernel has one positive charge, that of chlorine seven positive charges, etc.; but it may occasionally be desirable for pedagogical purposes to attach to the symbol of the atomic kernel, a small numeral as an index, to show the number of charges.

substances), reduction means an increase and oxidation a decrease in the number of electrons in the outer atom of the element. Thus for illustration, and with such reservations as will presently be shown necessary, we may state that chlorine has eight electrons in the outer shell in chlorides, six in hypochlorites, four in chlorites, two in chlorates and none in perchlorates.

Postulate 3 can best be illustrated by the use of formulae in which the electrons of the atomic shells are themselves considered as atoms of the element electricity¹ with the symbol **E**. Just as with ordinary symbols we use two types of formulae, one the gross formula representing hardly more than the chemical composition of the substance, the other a structural formula in which we attempt to represent the relative positions of the atoms, so we may, with the new symbols, employ the two types of formulae. We shall later discuss the structural formula, but at this point we may consider the gross formula involving the atomic kernels and the electrons of the outer atoms. Lithium has one positive charge in the kernel, fluorine has seven such charges, so that the neutral molecule of lithium fluoride we may represent LiFE_8 . In lithium sulfate **S** and **O** each has six positive charges, and $\text{Li}_2\text{SO}_4 = \text{Li}_2\text{SO}_4\text{E}_{24}$; $\text{SO}_4^{--} = \text{SO}_4\text{E}_{20}$. In every substance in which each element has either its highest or its lowest polar number, **E** will appear in multiples of 8. Thus $\text{NH}_3 = \text{NH}_3\text{E}_8$, $\text{H}_2\text{O} = \text{H}_2\text{OE}_8$, $\text{KOH} = \text{KOH}\text{E}_8$, $\text{NaNO}_3 = \text{NaNO}_3\text{E}_{24}$, $\text{AlO}_3\text{H}_3 = \text{AlO}_3\text{H}_3\text{E}_{24}$, $\text{MgCl}_2 = \text{MgCl}_2\text{E}_{16}$, $\text{K}_2\text{CO}_3 = \text{K}_2\text{CO}_3\text{E}_{24}$. In compounds in which the elements have polar numbers intermediate between the highest and the lowest the number of electrons is not as a rule a multiple of 8, but is in almost all cases *an even number*. Thus $\text{SO}_2 = \text{SO}_2\text{E}_{16}$, $\text{NaClO} = \text{NaClOE}_{14}$, $\text{C}_2\text{H}_2 = \text{C}_2\text{H}_2\text{E}_{10}$, $\text{C}_6\text{H}_6\text{O} = \text{C}_6\text{H}_6\text{OE}_{24}$.

The extraordinary generality of this rule is shown by the fact that among the tens of thousands of known compounds of the elements under consideration only a few exceptions are known. I may state here all of such compounds that are known to me as they form a very interesting class of substances. They all possess high reactivity and tend to go over into substances with an even number of electrons. First may be mentioned some of the elements themselves in the monatomic state, and as types we may take $\text{Na} = \text{NaE}$ and $\text{I} = \text{IE}_7$. In addition to these,² we have $\text{NO} = \text{NOE}_{11}$, $\text{NO}_2 = \text{NO}_2\text{E}_{17}$, $\text{ClO}_2 = \text{ClO}_2\text{E}_{19}$, $(\text{C}_6\text{H}_5)_3\text{C} = (\text{C}_6\text{H}_5)_3\text{CE}_{11}$, as well as other tri-aryl methyls³ and probably also the intensely colored

¹ Dr. Branch has kindly called my attention to a little book by Sir William Ramsay ("The Temple Primers; Modern Chemistry") in which he uses very similar formulae containing **E**.

² Possibly hypophosphoric acid is to be added to this list, but the evidence concerning its molecular weight does not seem conclusive.

³ See the review by Gomberg, *THIS JOURNAL*, 36, 1144 (1914).

compounds between alkali metals and di-aryl ketones,¹ and the colored substances which Wieland believes to contain bivalent and quadrivalent nitrogen.²

It is to be particularly noted that such substances when placed in a polar environment almost invariably change into substances with an even number of electrons in the outer atoms. Thus NO_2 dissolved in water gives nitrous and nitric acids, and even in pure liquid nitrogen tetroxide we must assume, since it has electrical conductivity, that such ions as $\text{NO}_2^+ = \text{NO}_2\text{E}_{16}$ and $\text{NO}_2^- = \text{NO}_2\text{E}_{18}$ are present. Similarly, ClO_2 dissolves to form chlorous and chloric acids to a small extent, triphenyl methyl dissolves in liquid sulfur dioxide to form a conducting solution with ions presumably of the type $(\text{C}_6\text{H}_5)_3\text{C}^+$ and $(\text{C}_6\text{H}_5)_3\text{C}^-$. Sodium in the metallic state, or when dissolved in such a solvent as liquid ammonia, dissociates according to the equation $\text{NaE} = \text{Na} + \text{E}$. In general, therefore, we may state that a substance, in whose gross formula an odd number of electrons appears, holds one electron by weak constraints, and in a medium which weakens all electric constraints, namely in a polar medium, the odd electron may be given up completely. Of the cases mentioned, the odd electron appears to be most firmly bound in NO , and even in a polar environment the constraints are still sufficiently powerful to hold the electron. Nevertheless in the presence of any oxidizing agent such as oxygen, that is, in the presence of a substance which has a strong tendency to take up an electron, the interchange will occur at once.

Molecules of this class which contain an odd or unpaired electron will for the sake of brevity be called *odd* molecules. An odd molecule will contain at least one atom with an uneven number of electrons in the shell. This may be called an *odd* atom.

Postulate 4 raises a question of the very greatest importance. Ever since the first suggestion of Helmholtz, numerous efforts have been made to explain chemical combination by the assumption that in the formation of a compound some of the electrons of one atom pass completely into another atom, and that the different charged parts of the molecule thus produced are held together by electrical forces. Such theories have, in my opinion, proved entirely inadequate except in the case of substances of the strongly polar type. This fact has been recognized by Thomson in his latest paper, in which he introduces an entirely different type of chemical combination in the case of the compounds which we have called nonpolar. However, according to the theory which I am now presenting, it is not necessary to consider the two extreme types of chemical combination, corresponding to the very polar and the very nonpolar compounds,

¹ Schlenk and Weickel, *Ber.*, 44, 1182 (1911).

² Wieland, *Ann.*, 381, 200 (1911); *Ber.*, 47, 2111 (1914).

as different in kind, but only as different in degree. This is due to the assumption of the interpenetrability of the atomic shells which is made in Postulate 4. Thus an electron may form a part of the shell of two different atoms and cannot be said to belong to either one exclusively. Hence in general it is impossible to say that one element in a compound has, during chemical change, been oxidized or reduced and that another element has not suffered such a change; but it is only as we approach substances of the completely polar type that such distinctions become less and less ambiguous. Since this question is one to which we shall frequently revert it need not be discussed further at this point.

Postulate 5 is based upon the fact that we do not find what might be called intra-atomic isomers. If the electrons of the atomic shell could at one time occupy one set of positions and at another time another set, and if there were no opportunity for ready transition from one of these sets of positions to another, we should have a large number of isomers differing from one another only in the situation of the electrons in the atomic shell. While there may possibly be a few cases where we might surmise the existence of just such isomers, in most cases it is evident that they do not exist, and we must assume, therefore, considerable freedom of change from one distribution of electrons in the shell to another.

Now there are only two ways in which one body can be held by another. It may, owing to a force of attraction, be drawn toward the second body until this force is gradually offset by a more rapidly increasing force of repulsion. In this case it comes to rest at a point where the net attraction or repulsion is zero, and is therefore in a condition of constraint with respect to any motion along the line joining the two centers; for if the distance between the two bodies is diminished they repel one another, while if the distance is increased they are attracted toward one another. An example of this type is a body attracted toward the earth but resting upon an elastic substance where the attractive force of gravity is offset by the repulsive force which we happen to call elastic; but it would be a mistake to consider the forces of elasticity to be different in character from other known forces. Indeed it is evident that just as we have the law of universal attraction between particles at great distances, so *at small distances* we have the equally universal *law of repulsion*.

The other way in which one body may hold another is that in which the planets are held by the sun, and this is the way that in some current theories of atomic structure the electrons are supposed to be held by the atom. Such an assumption seems inadequate to explain even the simplest chemical properties of the atom, and I imagine it has been introduced only for the sake of maintaining the laws of electromagnetics which are known to be valid at large distances. The fact is, however, that in the more prominent of these theories even this questionable advantage

disappears, for the common laws of electricity are not preserved. The most interesting and suggestive of these theories is the one proposed by Bohr¹ and based upon Planck's quantum theory. Planck in his elementary oscillator which maintains its motion at the absolute zero, and Bohr in his electron moving in a fixed orbit, have invented systems containing electrons of which the motion produces no effect upon external charges. Now this is not only inconsistent with the accepted laws of electromagnetics but, I may add, is logically objectionable, for that state of motion which produces no physical effect whatsoever may better be called a state of rest.

Indeed it seems hardly likely that much progress can be made in the solution of the difficult problems relating to chemical combination by assigning in advance definite laws of force between the positive and negative constituents of an atom, and then on the basis of these laws building up mechanical models of the atom. We must first of all, from a study of chemical phenomena, learn the structure and the arrangement of the atoms, and if we find it necessary to alter the law of force acting between charged particles at small distances, even to the extent of changing the sign of that force, it will not be the first time in the history of science that an increase in the range of observational material has required a modification of generalizations based upon a smaller field of observation. Indeed in the present case, entirely aside from any chemical reasons, a study of the mathematical theory of the electron leads, I believe, irresistably to the conclusion that Coulomb's law of inverse squares must fail at small distances.

In this connection I wish to call attention to an extremely interesting paper by Mr. A. L. Parson² which has only just been published, but which I had an opportunity of looking over with the author over a year ago. The fundamental assumption of Parson's theory is that the electron is not merely an electric charge but is also a small magnet, or, in his terminology, a magneton. Assuming therefore the existence of magnetic as well as electric forces between the different parts of the atom, Parson

¹ I believe that there is one part of Bohr's theory for which the assumption of the orbital electron is not necessary, since it may be translated directly into the terms of the present theory. He explains the spectral series of hydrogen by assuming that an electron can move freely in any one of a series of orbits in which the velocities differ by steps, these steps being simply expressed in terms of ultimate units (in his theory Planck's h is such a unit), and that radiation occurs when the electron passes from one orbital velocity to the next. It seems to me far simpler to assume that an electron may be held in the atom in stable equilibrium in a series of different positions, each of which having definite constraints, corresponds to a definite frequency of the electron, the intervals between the constraints in successive positions being simply expressible in terms of ultimate rational units (see Lewis and Adams, *Phys. Rev.*, 3, 92 (1914)).

² A "Magnetron Theory of the Structure of the Atom," *Smithsonian Publication* 2371, Washington, 1915.

was led entirely independently to the conclusion which I have stated above, namely that the most stable condition for the atomic shell is the one in which eight electrons are held at the corners of a cube. Not only in this but in a number of other important points the theory which I am presenting will be seen to coincide with that of Parson's paper. The results of the magnetic experiments with which he proposes to test the magneton theory will be of great interest. Meanwhile we may attempt to find, apart from any *a priori* consideration, just what atomic structure best explains known chemical facts.

There is one part of Parson's theory which agrees with my own former theory but which I now believe to be incorrect. The idea that argon is a system of concentric cubes (in Parson's theory cubes side by side), and that neon is a similar system with one less cube, led naturally to the assumption that helium is similarly constituted. But recent evidence from radioactive phenomena, and from Moseley's study of the X-ray spectrum, makes it seem almost certain that helium has a total not of eight but of either two or four electrons.¹ Assuming that helium is the only element between hydrogen and lithium and that it has two electrons, then it is evident from the inert character of helium, and from the resemblance of this element to the other inert gases, that here the pair of electrons plays the same role as the group of eight in the heavier atoms, and that in the row of the periodic table comprising hydrogen and helium we have in place of the rule of eight the rule of two. Therefore hydrogen not only has one electron in its outer shell, which may pass into the shell of another atom just as the electron of lithium or sodium may, but it is capable of taking up one electron to form the stable pair, just as fluorine or chlorine takes up one electron to form the stable group of eight. Hydrogen therefore must be regarded as the first member of the halogens as well as of the lithium group. According to this view lithium hydride is a salt² although perhaps less polar than lithium fluoride or chloride. Therefore in what follows we shall regard the acquisition of one additional electron by hydrogen as entirely analogous to the acquisition of enough electrons to form the group of eight in the case of other atoms.

Molecular Structure.

I shall now attempt to show how, by a single type of chemical com-

¹ Two, if hydrogen and helium are the only elements of lower atomic weight than lithium; four, if we assume with Rydberg that there are two rows in the periodic table, one containing hydrogen and proto-helium and one containing eka-hydrogen and helium. The above discussion will be the same on either of these assumptions, and although Rydberg's assumption has a very high degree of plausibility I have adopted for simplicity the more familiar one.

² In order to test this view experiments have been begun by Professor O. F. Stafford. These experiments have not progressed far but they at least indicate that fused lithium hydride is a good electrolyte.

bination, we may explain the widely varying phenomena of chemical change. With the original assumption of Helmholtz, which has been used by some authors under the name of the electron theory of valence, and according to which a given electron either does or does not pass completely from one atom to another, it is possible to give a very satisfactory explanation of compounds which are of distinctly polar type, but the method becomes less and less satisfactory as we approach the nonpolar type. Great as the difference is between the typical polar and nonpolar substances, we may show how a single molecule may, according to its environment, pass from the extreme polar to the extreme nonpolar form, not *per saltum*, but by imperceptible gradations, as soon as we admit that an electron may be the common property of two atomic shells.

Let us consider first the very polar compounds. Here we find elements with but few electrons in their shells tending to give up these electrons altogether to form positive ions, and elements which already possess a number of electrons tending to increase this number to form the group of eight. Thus Na^+ and Ca^{++} are kernels without a shell, while chloride ion, sulfide ion, nitride ion (as in fused nitrides) may each be represented by an atom having in the shell eight electrons at the corners of a cube.

As an introduction to the study of substances of slightly polar type we may consider the halogens. In Fig. 3 I have attempted to show the

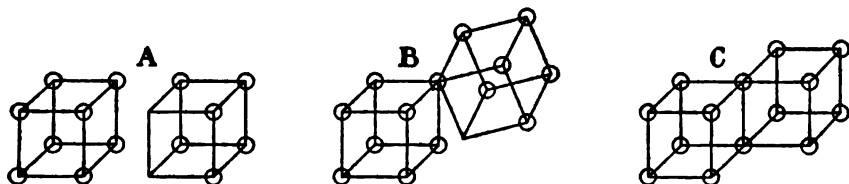


Fig 3.

different forms of the iodine molecule I_2 . A represents the molecule as completely ionized, as it undoubtedly is to a measurable extent in liquid iodine.¹ Without ionization we may still have one of the electrons of one atom fitting into the outer shell of the second atom, thus completing its group of eight as in B. But at the same time an electron of the second atom may fit into the shell of the first, thus satisfying both groups of eight and giving the form C which is the predominant and characteristic structure of the halogens. Now, notwithstanding the symmetry of the form C, if the two atoms are for any reason tending to separate, the two common electrons may cling more firmly sometimes to one of the atoms, sometimes to the other, thus producing some dissymmetry in the molecule as a whole, and one atom will have a slight excess of positive charge, the other of negative. This separation of the charges and the conse-

¹ See Lewis and Wheeler, *Loc. cit.*

quent increase in the polar character of the molecule will increase as the atoms become separated to a greater distance until complete ionization results.¹ Thus between the perfectly symmetrical and nonpolar molecule *C* and the completely polar and ionized molecule represented by *A* there will be an infinity of positions representing a greater or lesser degree of polarity. Now in a substance like liquid iodine it must not be assumed that all of the molecules are in the same state, but rather that some are highly polar, some almost nonpolar, and others represent all gradations between the two. When we find that iodine in different environments shows different degrees of polarity, it means merely that in one medium there is a larger percentage of the more polar forms. So bromine, although represented by an entirely similar formula, is less polar than iodine. In other words, in the average molecule the separation of the charge is less than in the case of iodine. Chlorine and fluorine are less polar than either and can be regarded as composed almost completely of molecules of the form *C*.

I wish to emphasize once more the meaning that must be ascribed to the term tautomerism. In the simplest case where we deal with a single tautomeric change we speak of the two tautomers and sometimes write definite formulae to express the two. But we must not assume that all of the molecules of the substance possess either one structure or the other, but rather that these forms represent the two limiting types, and that the individual molecules range all the way from one limit to the other. In certain cases where the majority of molecules lie very near to one limit or to the other, it is very convenient and desirable to attempt to express the percentage of the molecules belonging to the one or to the other tautomeric form; but in a case where the majority of molecules lie in the intermediate range and relatively few in the immediate neighborhood of the two limiting forms, such a calculation loses most of its significance.

With the halogens it is a matter of chance as to which of the atoms acquires a positive and which a negative charge, but in the case of a binary compound composed of different elements the atoms of one element will be positive in most, though not necessarily all, of the molecules. Thus in Br_2 the bromine atom is as often positive as negative, but in BrCl it will be usually positive and in IBr usually negative, although in all these substances which are not very polar the separation of charges in the molecule will be slight, whereas in the metallic halides the separation is nearly complete and the halogen atoms acquire almost complete possession of the electrons.

In order to express this idea of chemical union in symbols I would sug-

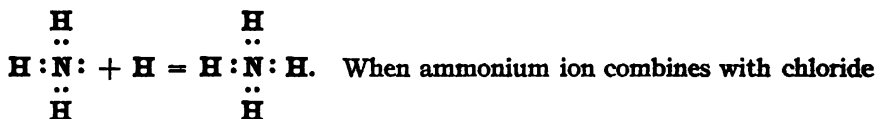
¹ When the separation occurs in a nonpolar environment the atoms may separate in such a way that each retains one of the two common electrons, as in the thermal dissociation of iodine gas.

gest the use of a colon, or two dots arranged in some other manner, to represent the two electrons which act as the connecting links between the two atoms. Thus we may write Cl_2 as $\text{Cl} : \text{Cl}$. If in certain cases we wish to show that one atom in the molecule is on the average negatively charged we may bring the colon nearer to the negative element. Thus we may write $\text{Na} : \text{I}$, and $\text{I} : \text{Cl}$. Different spacings to represent different degrees of polarity can of course be more freely employed at a black-board than in type.

It will be noted that, since in the hydrogen-helium row we have the rule of two in the place of the rule of eight, the insertion of one electron into the shell of the hydrogen atom is entirely analogous to the completion of the cube in the case of the halogens. Thus we may consider ordinary hydrogen as a hydride of positive hydrogen in the same sense that chlorine may be regarded as a chloride of positive chlorine. But H_2 is far less polar even than Cl_2 . The three main types of hydrogen compounds may be represented therefore by $\text{H} : \text{Cl}$, $\text{H} : \text{H}$, and $\text{Na} : \text{H}$.

We may go further and give a complete formula for each compound by using the symbol of the kernel instead of the ordinary atomic symbol and by adjoining to each symbol a number of dots corresponding to the number of electrons in the atomic shell. Thus we may write $\text{H} : \text{H}$, $\text{H} : \ddot{\text{O}} : \text{H}$, $\text{H} : \ddot{\text{I}} :$, $:\ddot{\text{I}}:\ddot{\text{I}}:$, but we shall see that in many cases such a formula represents only one of the numerous extreme tautomeric forms. For the sake of simplicity we may also use occasionally formulae which show only those electrons concerned in the union of two atoms, as in the preceding paragraphs.

It is evident that the type of union which we have so far pictured, although it involves two electrons held in common by two atoms, nevertheless corresponds to the single bond as it is commonly used in graphical formulae. In order to illustrate this point further we may discuss a problem which has proved extremely embarrassing to a number of theories of valence. I refer to the structure of ammonia and of ammonium ion. Ammonium ion may of course, on account of the extremely polar character of ammonia and hydrogen ion, be regarded as a loose complex due to the electrical attraction of the two polar molecules. However, as we consider the effect of substituting hydrogen by organic groups we pass gradually into a field where we may be perfectly certain that four groups are attached directly to the nitrogen atom, and these groups are held with sufficient firmness so that numerous stereochemical isomers have been obtained. The solution of this problem in terms of the theory here presented is extremely simple and satisfactory, and it will be sufficient to write an equation in terms of the new symbols in order to make the explanation obvious. Thus for $\text{NH}_3 + \text{H}^+ = \text{NH}_4^+$ we write



When ammonium ion combines with chloride ion the latter is not attached directly to the nitrogen but is held simply through electric forces by the ammonium ion.

While the two dots of our formulae correspond to the line which has been used to represent the single bond, we are led through their use to certain formulae of great significance which I presume would not occur to anyone using the ordinary symbols. Thus it has been generally assumed that what is known as a bivalent element must be tied by two bonds to another element or elements, or remain with an "unsaturated valence." On the other hand, we may now write formulae in which an atom of oxygen is tied by only one pair of electrons to another atom and yet have every element in the compound completely saturated. To illustrate this important point we may write the formula of perchlorate, sulfate, orthophosphate and orthosilicate ions, in which each atom has a

complete shell of eight electrons. Thus $\begin{array}{c} \vdots \ddot{\text{O}} : \\ \vdots \ddot{\text{O}} : \ddot{\text{X}} : \ddot{\text{O}} : \\ \vdots \ddot{\text{O}} : \end{array}$ represents all of

these ions. If X is Cl the ion has one negative charge; if S it has two negative charges, and so on. The union of sulfur trioxide to oxide ion to form sulfate ion is similar to the addition of ammonia and hydrogen ion to form ammonium ion. The acids or acid ions are produced from the above ion by adding hydrogen ion, or H , to the oxygen atoms.

We may next consider the *double bond* in which four electrons are held conjointly by two atoms. Thus Fig. 4, *A*, may represent the typical

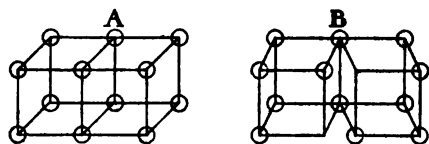


Fig. 4.

structure of the molecule of oxygen. A characteristic feature of the double bond is its tendency to "break." When this happens in a symmetrical way, as it will, except in a highly polar environment, it leaves

the two atoms concerned in the *odd* state, each with an unpaired electron in the shell. In so far as a substance with a double bond assumes this other tautomeric form, it will show all the properties of the substances with odd molecules. Thus Fig. 4, *B*, represents this tautomeric form of the oxygen molecule; the equilibrium between forms *A* and *B* is entirely analogous to the equilibrium between N_2O_4 and NO_2 . At low temperatures almost every known case of combination with oxygen gives first a peroxide. This shows that oxygen exists to an appreciable degree in a form which approximates to the form *B*, in which it can add directly to

other atoms precisely as ethylene forms addition compounds. These two forms of oxygen (which, of course, may merge into one another by continuous gradations) can be represented as $\ddot{\text{O}}:\ddot{\text{O}}:$ and $:\ddot{\text{O}}:\ddot{\text{O}}:$, and

$\begin{array}{ccc} \text{H} & \text{H} & \\ & & \text{H} & \text{H} \\ & & & & \\ \text{H}:\ddot{\text{C}}: & :\ddot{\text{C}}:\text{H} & \text{H}:\ddot{\text{C}}: & :\ddot{\text{C}}:\text{H} \end{array}$

the two forms of ethylene¹ as $\text{H}:\ddot{\text{C}}::\ddot{\text{C}}:\text{H}$ and $\text{H}:\ddot{\text{C}}:\ddot{\text{C}}:\text{H}$.

The instability of multiple bonds and the underlying principle of Baeyer's Strain Theory we shall discuss presently, but before proceeding further in this direction it is important to consider the general relation between the strength of the constraints which hold a molecule together and the stability of the molecule. The term "stability" is used in two very different senses, according as we think of the tendency of a reaction to occur, or the speed of that reaction. We speak of nitric oxide as an extremely stable substance although it is thermodynamically unstable, and the free energy involved in its decomposition is enormous, but it is so inert that it suffers no appreciable change. A high degree of inertness means ordinarily very rigid constraints operating within the molecule, but these powerful forces may operate only over a very small distance so that the *work* done in overcoming them may be very small. To illustrate this point let us consider a piece of iron suspended by a magnet. It is drawn downwards by the force of gravity and upwards by the magnetic field, and while the net amount of work obtained by separating it from the magnet and allowing it to fall to earth may be positive, it nevertheless will not fall of itself, but can only be drawn from the magnet by a force far greater than that of gravitation. So in the case of the molecule, thermodynamic stability is closely associated with the *work* of breaking some bond, but the inertness of the molecule depends upon the *force* required to break that bond.

Before considering triple bonds, for which the cubical structure offers no simple representation, I wish to discuss some ideas in the recent development of which I am greatly indebted to suggestions made by Dr. L. Rosenstein, Dr. E. Q. Adams and Mr. F. R. von Bichowsky, as well as to the work of Mr. A. L. Parson, to which I have already referred. In my early theory the cube was the fundamental structure of all atomic shells. We have seen, however, in the case of elements with lower atomic weights than lithium, that the *pair* of electrons forms the stable group, and we may question whether in general the pair rather than the group of eight should not be regarded as the fundamental unit. Perhaps the chief reasons for assuming the cubical structure were that this is the most symmetrical arrangement of eight electrons, and is the one in which the

¹ I shall postpone a discussion of the important bearing of such formulae upon the problem of the conjugate double bond.

electrons are farthest apart. Indeed it seems inherently probable that in elements of large atomic shell (large atomic volume) the electrons are sufficiently far from one another so that Coulomb's law of inverse squares is approximately valid, and in such cases it would seem probable that the mutual repulsion of the eight electrons would force them into the cubical structure.

However, this is precisely the kind of *a priori* reasoning which we have decided not to employ in this paper, and when we consider only known chemical phenomena, and their best interpretation in terms of atomic structure, we are led to assume a somewhat different arrangement of the group of eight electrons, at least in the case of the more nonpolar substances whose molecules are as a rule composed of atoms of small atomic volume.

The nature of this arrangement is shown in Fig. 5. The cube representing the electron structure that we have hitherto assumed for the carbon atom is joined to four other atoms, which are not shown in the figure, but which are attached to the carbon atom each by a pair of electrons. These pairs are indicated by being joined by heavy lines. Assuming now, at least in such very small atoms as that of carbon, that each pair of electrons has a tendency to be drawn together, perhaps by magnetic force if the magneton theory is correct, or perhaps by other forces which become appreciable at small distances, to occupy positions indicated by the dotted circles, we then have a model which is admirably suited to portray all of the characteristics of the carbon atom. With the cubical structure it is not only impossible to represent the triple bond, but also to explain the phenomenon of free mobility about a single bond which must always be assumed in stereochemistry. On the other hand, the group of eight electrons in which the *pairs* are symmetrically placed about the center gives identically the model of the tetrahedral carbon atom which has been of such signal utility throughout the whole of organic chemistry.

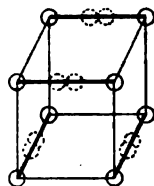


Fig. 5.

As usual, two tetrahedra, attached by one, two or three corners of each, represent respectively the single, the double and the triple bond. In the first case one pair of electrons is held in common by the two atoms, in the second case two such pairs, in the third case three pairs.

The triple bond represents the highest possible degree of union between two atoms. Like a double bond it may break one bond, producing two *odd* carbon atoms, but it may also break in a way in which the double bond cannot, to leave a single bond and two carbon atoms (bivalent), each of which has a pair of electrons which is not bound to any other atom. The three tautomeric forms may be represented in the case of

acetylene by $\text{H}:\text{C}:::\text{C}:\text{H}$, $\text{H}:\dot{\text{C}}::\dot{\text{C}}:\text{H}$, and $\text{H}:\ddot{\text{C}}::\ddot{\text{C}}:\text{H}$. In addition we have a form corresponding to Nef's acetylidene and such forms as may exist in highly polar media, such as the acetylide ion $:\text{C}:::\text{C}:\text{H}$.

The instability of multiple bonds, as well as the general phenomenon of ring formation in organic compounds is admirably interpreted by the Strain Theory of Baeyer. This theory may, however, be put into a far more general form if we make the simple assumption that *all atomic kernels repel one another*, and that molecules are held together only by the pairs of electrons which are held jointly by the component atoms. Thus two carbon atoms with a single bond strive to keep their kernels as far apart as possible, and this condition is met when the adjoining corners of the two tetrahedra lie in the line joining the centers of the tetrahedra. This is an essential element of Baeyer's theory of ring formation. When a single bond changes to a multiple bond and the two atomic shells have two pairs of electrons in common, the kernels are forced nearer together and the mutual repulsion of these kernels greatly weakens the constraints at the points of junction. This diminution in constraint therefore produces a remarkable effect in increasing the mobility of the electrons. In any part of a carbon chain where a number of consecutive atoms are doubly bound there is in that whole portion of the molecule an extraordinary reactivity and freedom of rearrangement. This freedom usually terminates at that point in the chain where an atom has only single bonds and in which therefore the electrons are held by more rigid constraints, although it must be observed that an increased mobility of electrons (and therefore increased polarity) in one part of the molecule always produces some increase in mobility in the neighboring parts.

Let us turn now to a problem in the solution of which the theory which I am presenting shows its greatest serviceability. The electrochemical theories of Davy and Berzelius were overshadowed by the "valence" theory when the attention of chemists was largely drawn to the nonpolar substances of organic chemistry. Of late the electrochemical theories have come once more into prominence, but there has always been that antagonism between the two views which invariably results when two rival theories are mutually exclusive, while both contain certain elements of truth. Indeed we may now see that with the interpretation which we are now employing the two theories need not be mutually exclusive, but rather complement one another, for the "valence" theory, which is the classical basis of structural organic chemistry, deals with the fundamental structure of the molecule, while electrochemical considerations show the influence of positive and negative groups in minor distortions of the fundamental form. Let us consider once for all that by a negative element or radical we mean one which tends to draw towards itself the electron pairs which constitute the outer shells of all neighboring atoms,

and that an electropositive group is one that attracts to a less extent, or repels, these electrons. In the majority of carbon compounds there is very little of that separation of the charges which gives a compound a polar character, although certain groups, such as hydroxyl, as well as those containing multiple bonds, not only themselves possess a decidedly polar character, but increase, according to principles already discussed, the polar character of all neighboring parts of the molecule. However, in such molecules as methane and carbon tetrachloride, instead of assuming, as in some current theory, that four electrons have definitely left hydrogen for carbon in the first case, and carbon for chlorine in the second, we shall consider that in methane there is a slight movement of the charges toward the carbon so that the carbon is slightly charged negatively, and that in carbon tetrachloride they are slightly shifted towards the chlorine, leaving the carbon somewhat positive. We must remember that here also we are dealing with averages and that in a few out of many molecules of methane the hydrogen may be negatively charged and the carbon positively.

In a substance like water the electrons are drawn in from hydrogen to oxygen and we have in the limiting case a certain number of hydrogen atoms which are completely separated as hydrogen ion. The amount of separation of one of the hydrogen atoms, and therefore the degree of ionization, will change very greatly when the other hydrogen atom is substituted by a positive or negative group. As a familiar example we may consider acetic acid, in which one hydrogen is replaced by chlorine, $\text{H}_3\text{CClCOOH}$. The electrons, being drawn towards the chlorine, permit the pair of electrons joining the methyl and carboxyl groups to approach nearer to the methyl carbon. This pair of electrons, exercising therefore a smaller repulsion upon the other electrons of the hydroxyl oxygen, permit these also to shift in the same direction. In other words, all the electrons move toward the left, producing a greater separation of the electrons from the hydrogen of the hydroxyl, and thus a stronger acid. This simple explanation is applicable to a vast number of individual cases. It need only be borne in mind that although the effect of such a displacement of electrons at one end of a chain proceeds throughout the whole chain, it becomes less marked the greater the distance,¹ and the more rigid the constraints which hold the electrons in the intervening atoms.

This brief account of the theory of atomic and molecular structure could be extended almost indefinitely by illustrations of its application to numerous types of compounds, but I believe enough has been said to show how,

¹ The distance to be considered is the *actual* distance. Thus when a chain of five or six links assumes a ring-like form, the two ends have a great influence upon each other, as has been pointed out by Michael in numerous cases.

through simple hypotheses, we may explain the most diverse types of chemical union and how we may construct models which illustrate the continuous transition between the most polar and the most nonpolar of substances. I shall therefore conclude this paper with a brief discussion of a phenomenon which bears closely upon the ideas which have been presented here.

The Color of Chemical Compounds.

When a particle is held in position by definite constraints, it is capable of vibrating with a definite frequency, and this frequency is determined solely by the magnitude of the constraints¹ and by the mass of the particle. When such a particle is electrically charged and subjected to the alternating electromagnetic forces which constitute a beam of light, and when the frequency of the light is near to the characteristic frequency of the particle, the latter is set to vibrating and through frictional processes the energy of the light is absorbed.

The two kinds of charged particles which exist in chemical substances are charged atoms and electrons. The former, on account of their relatively large mass, have low characteristic frequencies which are, as far as I am aware, always far below the frequencies of visible light and therefore cause absorption only in the ultrared spectrum. The electrons, on the other hand, because of their small mass and the rigid constraints by which they are ordinarily bound, usually have frequencies higher than those of visible light and therefore absorb light only in the ultraviolet. The majority of substances therefore show no special absorption of visible light and are therefore colorless.

When, however, either by a change in the constitution of the molecule or through a change in the environment, the constraints acting upon an electron become weaker, the frequency of that electron becomes less. It may then begin to absorb visible light of the highest frequency, namely the violet and blue, and the transmitted light is therefore yellow. Whenever a colorless substance becomes colored through slight changes by substitution of somewhat different groups within the molecule, or by gradual change in the environment, the substance is always *yellow*. But if the changes are made more pronounced and the characteristic frequency of the electron or electrons concerned is still further lowered, so that the maximum of absorption is in some other part of the visible spectrum, different colors will be produced, and ultimately when the electron is nearly freed from constraint, as in the case of an alkali metal dissolved in liquid ammonia, the maximum of absorption is in the ultra-red and red, and a blue color results.

¹ If the constraints are not uniform in all directions there will in general be three fundamental frequencies corresponding to the three axes of constraint, along which the constraints are respectively at a maximum, at a minimum and at a minimax.

Now colored substances are the very ones in which, according to our theory, the electrons are least firmly held. Thus such substances as nitrogen dioxide and sodium vapor, which contain an uneven number of electrons and which therefore hold one of the electrons very loosely, are colored. If, however, sodium combines with chlorine the electron becomes firmly held by the latter element and when nitrogen dioxide combines even with itself to form N_2O_4 the electron is again firmly held and the color disappears. Indeed, with the exception of NO, every one of the substances with odd molecules which we have listed is colored. The tri-aryl methyls show a remarkable analogy to NO_2 . In nonpolar media they show an increase of color when the conditions so change as to increase the amount of the monomolecular or odd molecules. Thus the color is increased by rising temperature or by increasing dilution, but the color of these substances in a polar environment is due to another cause, the discussion of which would lead us into the whole question of the triphenyl methane dyes.

Turning now to substances containing an even number of electrons, we see in the case of the halogens how the intensity and character of the color vary with the polar character. Thus the electrons which are concerned in the union of the two atoms of iodine are held by weaker constraints than in the case of bromine, and so on through the group. The electrons in fluorine, being most firmly held, absorb only the extreme violet end of the visible spectrum.

In general, color and a high degree of polarity go hand in hand, as is abundantly shown in the great class of organic dyes. Both of these phenomena are due to the same cause, namely the weakness of the constraints acting upon one or more electrons.

It has frequently been noticed that there is a striking parallelism between color and the possibility of tautomeric change, and it has been assumed by some that color is in some way due to an alternation between two extreme tautomeric forms. But this is not precisely the case. When electrons are sufficiently free to produce absorption in the visible spectrum, that part of the molecule in which they are will always be highly polar and reactive, and there will be opportunity for free transition from one limiting form to another. Thus if a tautomeric process consists chiefly in the movement of electrons, there will be electrons in some molecules which are hung by loose constraints between the two extreme forms, and these are the electrons which will have a sufficiently low characteristic frequency to produce color.

In the class of elements which have not been considered in the present paper many are found, such as manganese and cobalt, which give a great variety of colored compounds. The difficulty in interpreting the compounds of these elements in terms of the present theory lies, I believe,

in the fact that the kernel of the atom is not uniquely and permanently defined. It seems probable that in these elements there is a possibility of the transfer of electrons either from one part of the kernel to another, or between the kernel and the outer shell, or possibly between two separate outer shells of the same atom, and that electrons which are suspended midway between two such stages are responsible for the absorption of light in these cases.

BERKELEY, CAL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]
**A STUDY OF THE ACTION OF ALKALI ON CERTAIN ZINC SALTS
 BY MEANS OF THE HYDROGEN ELECTRODE.**

BY JOEL H. HILDEBRAND AND W. G. BOWERS.

Received January 24, 1916.

The reaction that occurs when zinc hydroxide is dissolved in a strong alkali has been the subject of considerable investigation. Carrara¹ has stated that the alkaline solution contains salts of the type Na_2ZnO_2 , making the hydroxide a dibasic acid. Förster and Günther² have obtained the solid compound $\text{NaHZnO}_2 \cdot 3\text{H}_2\text{O}$, and Comey and Jackson³ a solid compound having the formula $\text{Na}_2\text{Zn}_3\text{O}_5 \cdot 18\text{H}_2\text{O}$. We may mention also the solid alkaline earth zincates of the type $\text{Ca}(\text{HZnO}_2)_2$ reported by Bertrand.⁴ A number of investigators have endeavored to distinguish between the formulas ZnO_2^{--} and HZnO_2^- for the zincate ion. Perhaps the most reliable work is that of Hantzsch,⁵ who concludes that the zinc hydroxide is dissolved mainly as a colloid, but also to a slight extent as HZnO_2^- .

Most of the text-books on general chemistry state that the reaction for the solution of zinc hydroxide in alkali is given by the equation (here written in the ionic form)



in spite of the fact that the reaction represented by



is in much better accord with the evidence, and also with the usual behavior of weak polybasic acids. We find almost invariably that a second hydrogen atom ionizes much less readily than the first, as seen by the ease with which it is possible to prepare acid salts of such acids. It would be very strange, therefore, if the first main product of the neutralization of zinc hydroxide with sodium hydroxide were a solution of Na_2ZnO_2 .

¹ *Gazz. chim. ital.*, 30, II, 35 (1900).

² *Z. Elektrochem.*, 6, 302 (1899).

³ *Am. Chem. J.*, 11, 145 (1889).

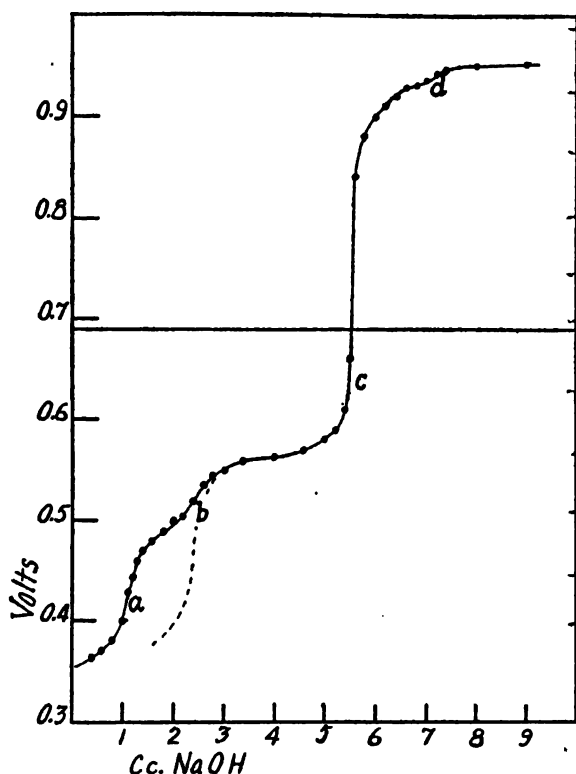
⁴ *Compt. rend.*, 115, 939, 1028 (1892).

⁵ *Z. anorg. Chem.*, 30, 289 (1902).

In a previous publication¹ on the general application of the hydrogen electrode, it was shown how clearly the reaction between aluminum hydroxide and alkali could be followed by this method. Instead of aluminum hydroxide being tribasic in its action towards alkali, as is so frequently stated in the text-books, it was shown to be monobasic.² The success of the hydrogen electrode in dealing with the constitution of aluminates has suggested its application to other amphoteric hydroxides.

The general method of procedure and the apparatus used have been explained in the earlier paper and the description will not be repeated here.

A large number of titrations were made with solutions of zinc halides containing usually an excess of the particular acid, and a few also with



solutions of zinc sulfate. The curves obtained with the solutions of zinc chloride, bromide, and iodide were so concordant that it is useless to repeat them all, and we represent one in the figure which may serve as an illustration of the whole series. At the beginning of the titration the solution had a volume of 100 cc. and contained 0.00044 mol of zinc, and about 0.0008 mol of HBr in excess. This was titrated with 0.287 N NaOH. The big rise in the curve at *c* corresponds to the completion of the precipitation of zinc hydroxide. We were much surprised to note the

extra inflection during the first portion of the curve at *a*, and found that it was pronounced only when there was an excess of acid in the solution. Furthermore, the portion of the curve from *a* to *b* represents one equivalent of alkali per mol of zinc, and the portion from *b* to *c* repre-

¹ Hildebrand, *THIS JOURNAL*, 35, 847, 1538 (1913).

² See also Blum, *Ibid.*, 35, 1499 (1913).

sents two equivalents. Since but two equivalents of alkali are needed to precipitate zinc hydroxide, and since the precipitate appears just a little before *b*, the only very obvious interpretation of the course of the curve from *a* to *b* is that this represents the neutralization of a weak acid having the composition HZnBr_2 . The presence of the ZnBr_2 makes one equivalent of HBr much weaker than it would otherwise be. Before the point *a* is reached we are neutralizing free HBr , acting as a strong acid, and if all of the excess HBr were free we would expect the curve up to *b* to follow approximately the dotted line in the figure, as was the case when zinc sulfate was used. This same peculiar behavior was found with each of the three halides, so that we feel justified in assuming the existence in solution of HZnCl_2 , HZnBr_2 , and HZnI_2 . Confirmation of this conclusion is found in the report by M. R. Engel¹ of solid compounds having the composition $\text{HZn}_2\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ and $\text{HZnCl}_3 \cdot 2\text{H}_2\text{O}$, both of which would fall between *a* and *b* on our curve. Since the position of this portion of the curve is nearly the same in each case, the three complex acids seem to be of about the same strength. The dissociation constant may be inferred roughly from the curve. A point half way from *a* to *b* represents equal concentrations of the acid and its ion, if the latter is not much dissociated into simpler ions, and hence the hydrogen ion concentration at this point equals the dissociation constant. Taking the corresponding e. m. f. as 0.48 volt, the hydrogen ion concentration, and also the dissociation constant, is about $4 \cdot 10^{-4}$.

We will now turn our attention to the portion of the curve from *c* to *d*. Though not very great, a well defined inflection is apparent at *d*. This means that the alkali is not free to exert its full effect in raising the e. m. f. till after *d* is passed, having been acted on before *d* by the zinc hydroxide. Since the amount of alkali used between *c* and *d* corresponds to one equivalent, it is obvious that the reaction here occurring is



The precipitate is not all dissolved at *d*, but this is not surprising, as the acid is so weak that a large excess of alkali must be present in order to make one equivalent of it react. The inflection at *d* can be shown mathematically to indicate that the amounts of acid and base are equivalent, even if neutralization is far from complete. There is no indication of the neutralization of the second hydrogen atom of the zinc hydroxide, and a very large excess of alkali must be necessary for it to take place even to a slight extent.

The solution is far from being clear at *d*, though the zinc hydroxide is usually in suspension at this point. The addition of alkali, therefore, must be regarded as doing two things, just as Hantzsch claims. Part of the alkali is adsorbed, changing the coagulum of zinc hydroxide to a

¹ *Compt. rend.*, 102, 1068 (1886).

suspension, and part of the alkali neutralizes the zinc hydroxide giving the acid zincate. That there is no very great distinction between these processes is evident when we consider that zinc hydroxide, like aluminum hydroxide, silicic acid, etc., is colloidal, so that its formula really is $(\text{H}_2\text{ZnO}_2)_n \cdot x\text{H}_2\text{O}$. It is hard to see any great distinction between the adsorption of OH^- by such a molecule, considered as a colloidal particle, on the one hand, and its gradual neutralization, considered as a polyacid, on the other hand. As the neutralization by OH^- (or adsorption of OH^-) proceeds, the molecule (or colloidal particle) becomes progressively smaller, until finally the acid zincate ion is produced. The solid polyzincate, $\text{Na}_2\text{Zn}_3\text{O}_5 \cdot 18\text{H}_2\text{O}$, reported by Comey and Jackson, is evidence in favor of this point of view. A similar relation undoubtedly exists between silicic acid and the silicates.

Summary.

There exists in solutions of zinc chloride, bromide and iodide, each containing an excess of the corresponding acid, a weak acid of the type HZnCl_2 .

Zinc hydroxide acts towards alkali essentially as a monobasic acid.

BERKELEY, CAL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE EXTRAPOLATION OF CONDUCTANCE VALUES.

BY MERLE RANDALL.

Received January 31, 1916.

In connection with researches upon the electrical conductivity of aqueous solutions, a function of the form $1/\Lambda = 1/\Lambda_0 + K(c\Lambda)^{n-1}$ has been very largely used in order to obtain the equivalent conductance, Λ_0 , at infinite dilution. In the above function Λ is the equivalent conductance at the concentration c , K is a constant, and n is a number which, for aqueous solutions, lies between 1.3 and 1.7. The value of n is so chosen that the graph obtained by plotting the values of $1/\Lambda$ against $(c\Lambda)^{n-1}$ is nearly a straight line, and two other graphs corresponding to neighboring values of n , on opposite sides of the first line, are also drawn so as to aid in determining the most probable point ($1/\Lambda_0$) at which the graphs cut the $1/\Lambda$ axis.¹

While the method outlined above enables one to obtain the best value for the equivalent conductance at zero concentration, the calculations are quite laborious, and unless the data are quite accurate and complete for the very dilute solutions, the result is somewhat uncertain.

¹ A. A. Noyes, *THIS JOURNAL*, 30, 335 (1908); J. Johnston, *Ibid.*, 31, 1010 (1909) discusses the use of the function and gives a plot which shows the general shape of the graphs obtained.

Noyes and Falk¹ have recently given accurate calculations of the Λ_0 value and percentage ionization² for a large number of salts by the above method. Abbott and Bray³ have shown that, if percentage ionization of a salt is plotted against its ion concentration, the ionization curves of salts of the same valence type do not intersect. The relation is more obvious if the percentage ionization is plotted, not against the ion concentration but against the square root of the ion concentration as in Fig. 1.

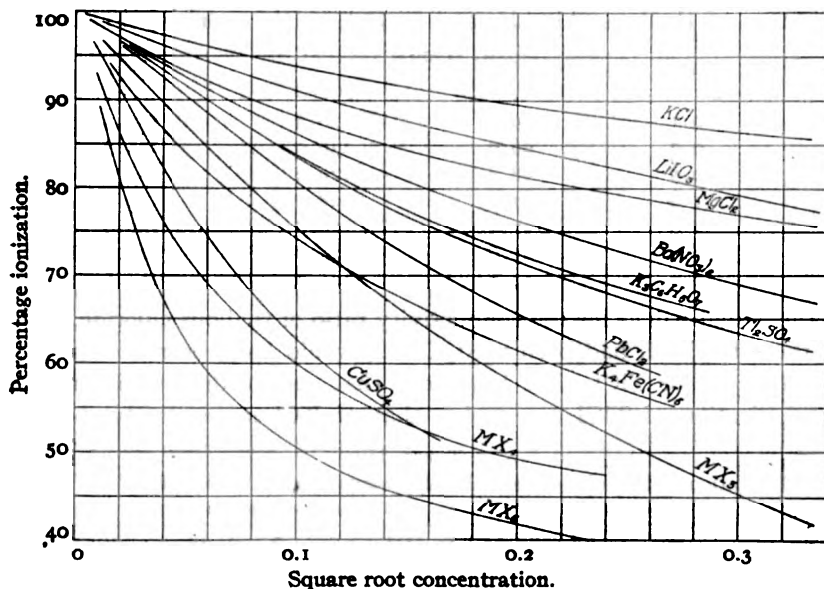


Fig. 1.—Percentage ionization of type salts.

It is also found that the salts of a single valence type divide themselves into several distinct groups. Thus, of the salts of the uni-univalent type in tenth molal solution, the chlorides, bromides and iodides of lithium, sodium, potassium, rubidium, caesium and ammonium are all ionized to about the same extent.⁴ The ionization of the nitrates, bromates and chlorates of the alkali metals, and of the halides of silver and thallium is several per cent. lower, and the ionization of silver nitrate and thallium nitrate is still several per cent. lower.

As the zero of concentration is approached the difference in the percentage ionization becomes smaller. If we may provisionally assume that the ionization of a salt such as thallos chloride is the same as that of a

¹ Noyes and Falk, *THIS JOURNAL*, 34, 454 (1912).

² The ionization is here defined by the conductance ratio Λ/Λ_0 . This definition is made for convenience. The validity of the extrapolation is independent of the assumption that the conductance ratio gives the true ionization.

³ Abbott and Bray, *THIS JOURNAL*, 31, 729 (1909).

⁴ Lewis, *Ibid.*, 34, 1631 (1912).

salt such as potassium chloride, the conductance of which has been carefully measured, and the Λ_0 value determined by any reliable method, as that mentioned above, the equivalent conductance at zero concentration is given by the usual equation

$$\Lambda_0 = \Lambda / \alpha$$

in which α is the degree of ionization.¹ Thus in Col. 2 of Table I is given the percentage ionization of potassium chloride at 18°, in Col. 3 the conductance of thallous chloride, and in Col. 4 the value of $\Lambda\text{TlCl}/\alpha\text{KCl}$.

TABLE I.

Millimols per liter.	100 α_{18° KCl.	Λ_{18° TlCl.	$\frac{\Lambda\text{TlCl}}{\alpha\text{KCl}}$
0.1	99.2	130.3	131.4
0.2	99.0	130.0	131.3
0.5	98.5	129.2	131.2
1.0	97.9	128.2	131.0
2.0	97.1	126.8	130.6
5.0	95.6	123.7	129.4
10.0	94.1	120.2	127.8

If the actual values for the conductivity ratio of thallous chloride, instead of those for KCl, had been used, Col. 4 would have been constant, and equal to Λ_0 for TlCl. We have seen that, as the dilution is increased, the ionization of TlCl approaches that of KCl more closely, becoming

TABLE II.

Ionization Values of Typical Salts of Various Valence Types at 18° (Λ/Λ_0).

Salt.	Milliequivalents per liter.									
	0.1.	0.2.	0.5.	1.	2.	5.	10.	20.	50.	100.
KCl.....	99.2	99.0	98.5	97.9	97.1	95.6	94.1	92.2	88.9	86.0
LiIO ₃	99.1	98.7	97.9	97.0	95.8	93.6	91.2	88.3	83.4	78.9
MgCl ₂	98.4	97.8	96.7	95.5	93.9	91.0	88.3	85.1	80.3	76.5
Ba(NO ₃) ₂	98.4	97.8	96.7	95.3	93.4	89.8	86.1	81.8	74.4	67.9
Tl ₂ SO ₄	(96.4)	94.8	92.4	88.2	83.7	78.0	69.4	62.5
PbCl ₂	(96.0)	94.3	91.7	86.5	80.8	73.8	62.7	..
K ₃ C ₆ H ₅ O ₇	96.4	94.8	92.6	88.2	81.7 ²	..	70.5	..
MX ₃ ³	94.5	92.2	88.6	82.3	75.5	67.0	54.1	43.8
K ₄ Fe(CN) ₆	85.9	..	71.2 ²	..	59.1	..
CuSO ₄	96.1	94.4	90.5	86.2	80.4	70.9	62.9	55.0
MX ₄ ⁴	90.1	83.9 ⁵	..	74.2	64.2 ⁶	..	54.3	48.1	..
MX ₅ ⁷	85.2	77.2 ⁵	..	65.2	55.0 ⁶	..	45.6	40.3	..

¹ Noyes and Falk, *THIS JOURNAL*, 34, 455 (1912).

² 12.5 millinormal.

³ No accurate determination of the conductance of salts of this type is available. Theoretical values in which $1 - \alpha$ for a salt of this type was considered equal to $3/2(1 - \alpha)$ for Tl₂SO₄ have been found very useful.

⁴ Tetra sodium benzene pentacarboxylate. Noyes and Lombard, *THIS JOURNAL*, 33, 1423 (1911).

⁵ 0.6 millinormal.

⁶ 6.0 millinormal.

⁷ Penta sodium benzene pentacarboxylate.

equal at infinite dilution. If, then, we plot the values of $\Delta\text{TlCl}/\alpha\text{KCl}$ against the ion concentration, or, better, against the square root of the ion concentration, and extrapolate this curve graphically to zero concentration we will obtain for TlCl $\Lambda_{0,18^\circ} = 131.4$. Noyes and Falk found 131.4. Even in the case of very accurate data a rough plot will suffice to give an accurate extrapolation.

The ionization values at 18° calculated by Noyes and Falk for a number of typical salts of the various valence types are given in Table II.

The examples given in Table III will illustrate the extreme simplicity of the method outlined above.

TABLE III.

Millequivalents per liter.	$\frac{\Lambda_{18}^\circ \text{LiIO}_3}{c_{18}^\circ \text{KCl}}$	$\frac{\Lambda_{18}^\circ \text{Ba}(\text{BrO}_3)_2}{c_{18}^\circ \text{Ba}(\text{NO}_3)_2}$	$\frac{\Lambda_{18}^\circ \text{K}_2\text{SO}_4}{c_{18}^\circ \text{Ba}(\text{NO}_3)_2}$	$\frac{\Lambda_{18}^\circ \text{K}_2\text{SO}_4}{c_{18}^\circ \text{MgCl}_2}$	$\frac{\Lambda_{18}^\circ \text{Mg}(\text{NO}_3)_2}{c_{18}^\circ \text{Ba}(\text{NO}_3)_2}$	$\frac{\Lambda_{18}^\circ \text{Mg}(\text{NO}_3)_2}{c_{18}^\circ \text{MgCl}_2}$	$\frac{\Lambda_{18}^\circ \text{La}(\text{NO}_3)_3}{c_{18}^\circ \text{K}_2\text{Cr}_2\text{O}_7}$
1	66.7	119.3	125.4	125.3
2	66.4	119.1	155.1	154.4	125.7	125.0	139.2
5	65.9	119.1	155.7	153.7	126.8	125.1
10	65.2	119.3	156.3	152.3	128.1	125.0
20	64.4	118.9	156.9	150.8	129.7	124.6	140.0
50	63.1	159.3	147.5	134.1	124.3	141.4

The Λ_0 value calculated by this new method for LiIO_3 , using KCl as the reference salt, was 67.3, in agreement with the value calculated by Noyes and Falk. For $\text{Ba}(\text{BrO}_3)_2$ Λ_0 is 119.2, while the longer method gives 120.0. When K_2SO_4 is compared with $\text{Ba}(\text{NO}_3)_2$ Λ_0 is 154.0, with MgCl_2 Λ_0 is 155.4, mean 154.7. Noyes and Falk found 154.8. Likewise, $\text{Mg}(\text{NO}_3)_2$ compared with $\text{Ba}(\text{NO}_3)_2$ gave $\Lambda_0 = 124.4$, and with MgCl_2 $\Lambda_0 = 125.4$. The last result is entitled to much greater weight, since the variation of the latter ratio is much smaller, hence Λ_0 is taken as 125.3. Noyes and Falk found $\Lambda_0 = 125.6$. In the case of $\text{La}(\text{NO}_3)_3$ the new value 138.6 is certainly much nearer the correct value than that of Noyes and Falk, namely, 142.6.

In general, that salt is chosen for the reference salt which makes the provisional value of Λ_0 most nearly constant. In some cases it is advisable to choose several reference salts, and take the average. It is not necessary that the reference salt be chosen at the same temperature, for the ionization curves do not cross as the temperature is changed. It will often be possible by the aid of three or four points to determine a fairly accurate value of Λ_0 , as in the case of $\text{La}(\text{NO}_3)_3$.

In a large number of papers published recently¹ the percentage dissociation has been calculated from the equation $100\alpha = 100\mu/\mu_\infty$ where μ_∞ is the highest value of μ (Siemen's units²) measured, obtained sometimes at

¹ Watkins and Jones, *THIS JOURNAL*, 37, 2626 (1915).

² The use of the obsolete Siemen's units for expressing conductance data leads to

1024, and sometimes at 2048 and 4096 liters. These "percentage ionizations" obviously have no significance since the values of μ_{∞} (reduced to mhos) are in no case as large as Λ_0 obtained by any method of extrapolation. The divergence is greatest in the case of polyionic salts. Moreover, conductivity measurements are in most cases unreliable at these extreme dilutions. In the papers cited the equivalent conductance at 2048 liters is often less than at 1024 liters. The method outlined in the present paper will enable one rapidly to extrapolate conductance values and in the case of inconsistent and incomplete data to obtain approximately correct percentage ionization values.

BERKELEY, CAL.

A STUDY OF THE LEAD ELECTRODE.

BY FREDERICK H. GETMAN.

Received February 1, 1916.

The present paper contains a brief summary of the results of a series of experiments carried out with a view to determining the constancy and reproducibility of the lead electrode. The methods employed are essentially those described in previous papers dealing with the reproducibility of the copper electrode¹ and the reproducibility of the cadmium electrode.² In both of these papers it was pointed out that the variations observed in the potential of electrodes cast or drawn from the metals under investigation were most satisfactorily explained on the ground of allotropism. The recent studies of Cohen and his co-workers³ on the metastability of the metals, has established the existence of metallic allotropes beyond any question.

Evidence of the allotropism of lead has been adduced by Heller⁴ who observed that when a piece of freshly cast, pure lead was immersed in a solution of lead acetate, acidified with nitric acid, it gradually underwent transformation into a gray modification, the change being complete in about three weeks. This gray modification was found to be brittle much confusion. Electrical measuring instruments as now manufactured are calibrated in international ohms and not in Siemen's ohms. In the paper of Watkins and Jones references are given to numerous other papers from the Johns Hopkins Laboratory in which Siemen's units are used. In the most recent article (Lloyd, Wiesel and Jones, *THIS JOURNAL*, 38, 121 (1916)) the conductances are presumably in Siemen's units although it is not so stated by the authors. In general, investigators both here and abroad use international ohms.

¹ Getman, *Trans. Am. Electrochem. Soc.*, 26, 67 (1914).

² Getman and Gibbons, *THIS JOURNAL*, 37, 953 (1915).

³ Cohen, *Verslag Akad. Wetenschappen*, 16, 485, 565, 628, 632, 807 (1913-14); 17, 54, 59, 60, 122, 200 (1914); 23, 754, 896 (1914); 23, 1220 (1915); 18, 91 (1915); *Z. physik. Chem.*, 85, 419 (1913); 87, 409, 419, 426, 431 (1914); 89, 493, 728, 733, 742, 748, 757 (1915); *Trans. Faraday Soc.*, 10, 216 (1915).

⁴ *Z. physik. Chem.*, 89, 761 (1915).

and easily reduced to a powder by pressure between the fingers. He also pointed out that the change takes place in solutions of lead nitrate and lead chloride, and that the transformation is accelerated by the addition of a small amount of nitric acid.

Furthermore, there is no change if lead is immersed in solutions of nitric acid, acetic acid or sodium acetate alone, thus proving that the transformation into the gray modification is due to the lead ions furnished by the lead salt. In a private communication to Prof. Cohen, Heller described an experiment in which a solution of lead acetate, acidified with nitric acid, was electrolyzed between lead electrodes in order to obtain a lead tree. After standing for three weeks, the electrodes were found to have crumbled to a grayish powder.

Upon inoculating a piece of freshly cast pure lead with some of the powder obtained in this experiment and immersing it in an acidified solution of lead acetate, Heller observed that the plate underwent rapid disintegration.

These results have since been confirmed by Cohen and Helderman¹ and also by the author.

Cohen and Helderman also noted that it is possible to produce a lead tree by immersing pure metallic lead in an acidified solution of lead acetate or in a 30% solution of lead nitrate, the rapidity of growth being increased by rise of temperature.

Similar results have recently been obtained by Creighton² by electrolyzing a solution of nitric acid (sp. gr. 1.42) between lead electrodes, employing a current of $N. D._{100} = 12.5$ amperes at 6 volts. At the end of eight hours, when the current was stopped, an examination of the cathode showed that it had lost the characteristic properties of lead and had become transformed into a gray mass which could be easily powdered between the fingers. This modification of lead appears to be identical with that obtained by Heller and Cohen.

The investigations of Cohen and Helderman³ with the pycnometer and the dilatometer make it appear highly probable that more than two allotropic modifications of lead are present in freshly cast specimens of the metal. This is shown by the following data taken from Cohen's papers: The density of a freshly cast specimen of lead was found to be $d_{4}^{25^{\circ}} = 11.324$. The metal was then immersed in Heller's solution (400 g. lead acetate in 1000 cc. of water to which is added 100 cc. of nitric acid (sp. gr. 1.16)) and allowed to stand for three weeks at a temperature of 15° . The density was now found to have increased to 11.341. On repeating the experiment at 50° and allowing the metal to remain immersed

¹ *Verslag Akad. Wetenschappen*, 17, 822 (1915).

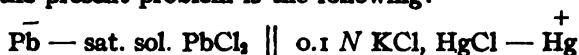
² Creighton, *THIS JOURNAL*, 37, 2064 (1915).

³ *Loc. cit.*

in the solution for five days, the density *decreased* to 11.313. Further immersion in the solution for six days at 25° caused the density to *increase* to 11.328. The following results were obtained by Cohen with the dilatometer: At 50.8° there was a *fall* of 700 mm. in 34 hours, whereas at 74.4° there was a *rise* of 275 mm. in 2 $\frac{3}{4}$ hours. In view of these results it seemed highly probable that electrodes of freshly cast lead would be more or less unstable and that, as in our previous work on copper and cadmium, a constant and reproducible lead electrode must be sought in a form of the metal which is stable under ordinary laboratory conditions.

Outline of Method.

Numerous galvanic combinations have been employed in studying the electromotive behavior of lead, but the one which seemed to be best adapted to the present problem is the following:



A cell very similar to this was used by Abegg and Labendzinski¹ in an investigation of the constitution of salts, the lead electrode consisting of an electrolytic deposit of lead on a platinum wire and the calomel electrode being made up with *N* KCl. The electromotive force of the cell at room temperature was found to be 0.456 volt.

In the present investigation the lead electrode was prepared in a variety of different ways, with a view to determining the most constant and reproducible form. The study of the electrochemical behavior of the different lead electrodes was supplemented by microscopical examination as in our previous work on cadmium electrodes.

Preparation of Materials.

The lead used in this investigation was obtained from two different but equally reliable firms. It was purified with great care and its purity was tested by spectroscopic examination with a Hilger spectrograph. The only foreign metal which could be detected was a trace of molybdenum. The saturated solution of lead chloride was prepared by precipitating a solution of pure lead nitrate with hydrochloric acid, washing by decantation with cold distilled water until nearly free from acid and then finally washing on the filter with 95% alcohol. The lead chloride so obtained was transferred to a bottle and shaken with distilled water at 25°, thus insuring a saturated solution at the temperature at which the electromotive measurements were to be carried out. The calomel electrode was prepared in the usual manner, care being taken to use only the purest materials and to secure a 0.1 *N* KCl solution completely saturated with calomel.

¹ *Z. Elektrochem.*, 10, 77 (1904).

Apparatus.

The measurements of electromotive force were made by the familiar compensation method, using a Wheatstone bridge and enclosed type of capillary electrometer sensitive to 0.0001 volt as a null instrument.

The standard cell used was of the Weston type and was frequently compared with a cell recently standardized by the Bureau of Standards. All comparisons of the Weston cell with the laboratory standard cell were made by means of a potentiometer reading to 0.00001 volt.

The experimental cell was similar to that used by Gibbons and Getman¹ in their study of nonaqueous solutions of silver nitrate.

The lead electrodes were prepared in five different ways, as follows: (1) Casting the purified lead in sticks 3 mm. in diameter and 7 cm. long; (2) amalgamating cast stick electrodes; (3) depositing lead electrolytically on spirals of platinum wire; (4) depositing lead electrolytically on cast stick electrodes; and (5) immersing stick electrodes in an acidified solution of lead acetate (Heller's solution).

The amalgamated electrodes were obtained by rubbing mercury over the lead sticks with a piece of filter paper.

Considerable difficulty was experienced in securing an adhesive deposit of lead on the platinum spirals. After trying various methods, very satisfactory results were obtained by using, as an electrolytic bath, a 10% solution of lead nitrate containing 5% glacial acetic acid and 1% of Barbadoes aloes, as recommended by Mathers and McKinney.² The platinum spirals were made by coiling 3 cm. of No. 28 wire (B. and S. gauge) around the apex of a filter cone and then flattening the resulting conical spiral on a plane surface. Each of these spirals was made, in turn, the cathode of an electrolytic cell, in which a piece of pure lead served as the anode. A current of 20 milliamperes at 2 volts was passed for 30 minutes, at the end of which time a gray adherent deposit of lead was obtained. The same procedure was followed in depositing lead electrolytically upon the lead sticks.

All of the volumetric apparatus employed was carefully calibrated. The temperature of the cells was maintained constant to within 0.01° by means of an electrically heated thermostat having a capacity of 55 liters.

Experimental Results.

Two entirely independent series of experiments were carried out in the investigation of the electromotive behavior of lead. The materials used in making up the cells for the two series were derived from different sources and were subjected to separate processes of purification. In

¹ THIS JOURNAL, 36, 1645 (1914).

² *Trans. Am. Electrochem. Soc.*, 27, 131 (1915).

Tables I, II, III, IV and V are given the results obtained with cells made up according to the following scheme:

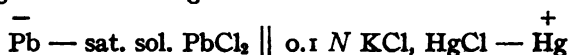


TABLE I.—FRESHLY CAST ELECTRODE.

T. (hrs.).	E. M. F. volt.
..	0.5206
2.5	0.5203
3.5	0.5201
4.0	0.5194
23.5	0.5198
24.0	0.5204
27.0	0.5210
28.0	0.5203
46.0	0.5196

Mean, 0.5202

TABLE II.—AMALGAMATED ELECTRODE.

T. (hrs.).	E. M. F. volt.
...	0.5178
0.75	0.5191
3.0	0.5196
4.0	0.5177
5.0	0.5188
24.5	0.5186
27.25	0.5134
72.0	0.5183

Mean, 0.5186

TABLE V.—ELECTROLYTIC LEAD ON PLATINUM.

T. (hrs.).	E. M. F. volt.
...	0.5221
0.5	0.5216
1.0	0.5228
2.25	0.5236
19.0	0.5219
20.25	0.5214
21.25	0.5223
24.0	0.5216
25.5	0.5221
41.5	0.5204
45.75	0.5214
50.0	0.5201
65.5	0.5225

Mean, 0.5218

TABLE III.—ELECTROLYTIC LEAD ON LEAD

T. (hrs.).	E. M. F. volt.
..	0.5231
0.5	0.5222
1.0	0.5226
3.0	0.5227
4.5	0.5224
23.0	0.5226

Mean, 0.5226

TABLE IV.—STICK ELECTRODE IMMERSED FOR 17 DAYS IN HELLER'S SOLUTION.

T. (hrs.).	E. M. F. volt.
...	0.5327
0.25	0.5302
1.00	0.5301
17.75	0.5306
20.0	0.5301
22.5	0.5327

Mean, 0.5310

TABLE VI (FIRST SERIES).

Freshly cast electrodes.

Observations.	Time (hrs.).	E. M. F. volt.
10	46.0	0.5202
7	24.0	0.5194
7	24.5	0.5190

Mean, 0.5195

Lead on lead electrodes.

6	23.5	0.5217
6	23.0	0.5226

Mean, 0.5221

Amalgamated electrodes.

Observations.	Time (hrs.).	E. M. F. volt.
8	28.5	0.5204
10	29.7	0.5170
8	72.0	0.5186

Mean, 0.5187

Lead on platinum.

6	48.0	0.5212
5	23.5	0.5218

Mean, 0.5215

Stick electrodes treated with Heller's soln.

Observations.	Time (hrs.).	E. M. F. volt.
12	95.5	0.5252 ¹
9	52.75	0.5283 ¹
11	114.4	0.5277 ¹
9	71.0	0.5267 ²
10	96.0	0.5271 ²
6	335.5	0.5239 ⁴

Mean, 0.5265

¹ 3 weeks' immersion in Heller's solution.

² 6 days' immersion in Heller's solution.

³ 8 days' immersion in Heller's solution.

⁴ Electrode cast from lead disintegrated by Heller's solution.

The character of the lead electrode was varied as indicated in each table. The temperature at which all of the cells were maintained was $25^{\circ} \pm 0.01^{\circ}$. In the first column of the tables is given the interval of time, T , which elapsed since the initial measurement at the moment when the cell was immersed in the bath, and in the second column is given the electromotive force. The probable error of these measurements is about 0.1%.

A summary of the results of the two series of experiments is given in Tables VI and VII.

TABLE VII (SECOND SERIES).

Freshly cast electrodes.			Lead on platinum.			Electrodes treated with Heller's soln.		
Observations.	T. (hrs.).	E. M. F. volt.	Observations.	T. (hrs.).	E. M. F. volt.	Observations.	T. (hrs.).	E. M. F. volt.
8	69.25	0.5183	9	27.75	0.5221	10	51.0	0.5200 ¹
10	42.25	0.5200	10	74.5	0.5218	7	43.5	0.5274 ¹
			13	65.5	0.5218	6	21.0	0.5193 ³
				5.9	0.5218	6	22.0	0.5310 ³
	Mean,	0.5192				8	20.1	0.5304 ⁴
				Mean,	0.5219			Mean, 0.5256

Discussion of Results.

An examination of the foregoing tables brings out the fact that while there is very little difference between the potentials of the five types of lead electrode studied, yet the most constant and reproducible is the electrode formed by deposition of lead on platinum. Contrary to our expectation the widest variation occurred with the lead sticks which had been immersed for different periods of time in Heller's solution. The experiments would seem to indicate that immersion in Heller's solution tends to make the lead electrode more negative. The change in potential, however, is not proportional to the time of immersion, as is shown by the experiment of Series II where an electromotive force of 0.5304 volt was obtained after eleven days' immersion in Heller's solution, whereas an immersion of three weeks in Series I developed an electromotive force of only 0.5283 volt.

The electromotive force of cells in which the lead electrode had been immersed in Heller's solution almost invariably diminished rapidly and came to constancy at about 0.5220 volt. The subjoined table gives a series of typical results.

TABLE VIII.

T. (minutes).....	0	10	20	40	50	60
E. M. F. volt.....	0.5304	0.5252	0.5232	0.5224	0.5220	0.5220

- 1 1 week's immersion in Heller's solution.
2 3 days' immersion in Heller's solution.
3 17 days' immersion in Heller's solution.
4 11 days' immersion in Heller's solution.

On representing the data of this table graphically, plotting time on the axis of abscissae and logarithms of electromotive force on the axis of ordinates, it was found that the relationship between these two variables was not rectilinear, as should be the case if the change in electromotive force were due to the transition of one modification of lead into the other.

Furthermore, if the gray modification of lead is stable at ordinary temperatures, there should be no change in the electromotive force of a cell of which it forms a part.

In his recent lecture before the Faraday Society, Cohen¹ says:

"It is generally known that when a bar of any metal which is more electronegative than lead is suspended in a solution of a lead salt, the lead is thrown out of solution and a lead tree is formed."

He then states that the same phenomenon occurred when a stick of pure lead was placed in Heller's solution or in a neutral solution of lead nitrate, the tree being formed within a few days at room temperature or more rapidly at higher temperatures. If the gray form of lead which separates on the surface of a stick of pure lead when immersed in Heller's solution, is identical with Cohen's lead tree, and hence is more positive than the freshly cast metal, then the electromotive force of a cell in which the gray modification forms the negative electrode should be less than the electromotive force of a cell in which the negative electrode consists of freshly cast lead. The results given in Tables VI and VII fail to confirm this prediction based on Cohen's statement, and furthermore, all of the attempts made with the lead used in these experiments to develop a tree in Heller's solution or in a solution of lead nitrate have failed. Additional experiments on cells involving the gray modification of lead were made with the following combination:

Pb (freshly cast) — 0.2 N Pb(NO₃)₂ — Pb (gray)

The gray electrode was formed by immersing a freshly cast stick of lead in Heller's solution for two weeks. According to the data of Tables VI and VII, the electromotive force of such a cell at 25° should be about 7 millivolts, the current flowing outside of the cell from the freshly cast to the gray electrode. In Table IX is given the results of one of several experiments made with the above cell, a sensitive potentiometer having been employed to measure the minute electromotive forces developed.

TABLE IX.
Temp. 25°.

T. (hrs.).....	0	0.5	1	2	3	4	5	6	7.5	9.5	21.5
E. M. F. millivolts	5.065	1.775	1.415	1.170	1.090	1.003	0.760	0.555	0.292	-0.068	-0.125

The initial value of the electromotive force is about 2 millivolts less than the predicted value, but this discrepancy may be ascribed to the rapidity with which the electromotive force is falling. It will be noticed that

¹ *Loc. cit.*

after nine hours the polarity of the cell underwent a reversal, which suggests that a transition may have taken place in one of the electrodes. Unfortunately, attempts to duplicate these results proved quite fruitless and experiments of a similar nature carried out at the temperature of melting ice failed to reveal any change in the relative stability of the two forms of lead. In some cases rapid reversals of the polarity of the cell occurred, but this phenomenon is probably connected with surface strains in the freshly cast electrode.

On repeating the experiments with electrolytic lead electrodes the results were quite as unsatisfactory as when freshly cast sticks were employed. Thus, it is evident that, until some definite knowledge is obtained as to the limits of stability of the allotropic forms of lead and methods are developed for their isolation in a pure form, the exact value of the potential of a lead electrode, reproducible and constant at ordinary temperatures, cannot be obtained. The foregoing experiments indicate, nevertheless, that when lead is deposited electrolytically on platinum a *practically* reproducible and constant electrode is secured.

From the data of Tables VI and VII it is possible to compute the normal potential of the lead electrode. According to Nernst, the relationship between the potential of a single electrode and the concentration of the electrolyte is given by the equation

$$E_p = E - \frac{RT}{nF} \log_e C\alpha,$$

where E_p is the difference of potential between the electrode and a normal solution of ions furnished by the electrode, E the potential of the electrode in the given cell, C the concentration of the electrolyte, α the degree of ionization of the electrolyte, R the gas constant, T the absolute temperature, n the valence of the ion furnished by the electrode and F the faraday equivalent = 96,540 coulombs.

From the data compiled by Boettger¹ for difficultly soluble salts we obtain the following values for the normal concentration of a saturated solution of lead chloride and its degree of ionization: $C = 0.0692$ and $\alpha = 0.956$. Although these values were obtained at 18° it may be assumed that the corresponding data for 25° will not differ enough to prohibit their use in calculating the normal electrode potential of lead.

Since the potential of the calomel electrode with $0.1\ N\ KCl$ at 25° is 0.6186 volt, the potential of the lead electrode is $0.6186 - 0.5217 = 0.0969$ volt. Substituting in the above equation, we have

$$\begin{aligned} E_p &= 0.0969 - \frac{0.0591}{2} \log_{10} (0.0692 \times 0.956) \\ &= 0.1318 \text{ volt at } 25^\circ. \end{aligned}$$

¹ *Z. physik. Chem.*, 46, 521 (1903).

The value of the normal electrode potential of lead as given by the Deutsche Bunsen Gesellschaft is 0.129 volt at 18°.

The electrodes used in the preceding experiments were examined microscopically and numerous photomicrographs were made to facilitate further study of surface characteristics, particular attention being given to lead immersed in Heller's solution. The rapidity with which a piece of freshly cast lead undergoes transformation into the gray modification is well illustrated by the accompanying photomicrographs. Owing to the difficulty of securing a polished lead surface, the molten metal was cast in a mold, the bottom of which consisted of a piece of steel polished to a plane surface. In this way it was possible to secure a satisfactory mirror-like surface of lead. In Fig. 1 is shown such a surface under a magnifica-

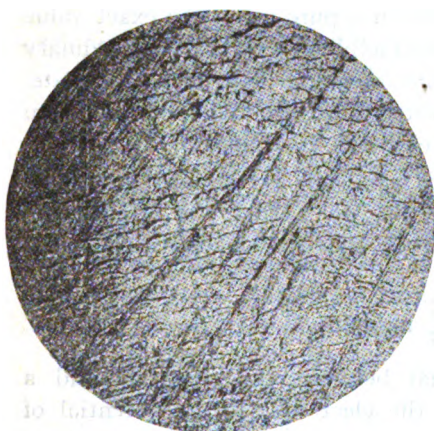


Fig. 1.—Mag. 190.

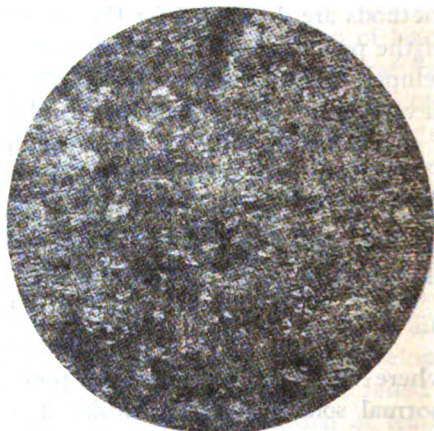


Fig. 2.—Mag. 190.

tion of 190 diameters. This piece of lead was then immersed in Heller's solution and allowed to stand at room temperature for twenty-four hours.

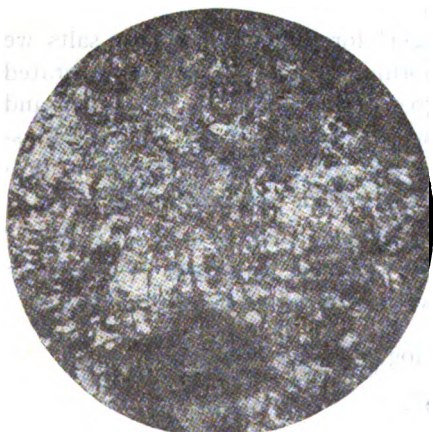


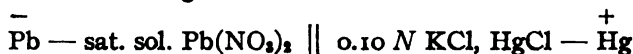
Fig. 3.—Mag. 190.

It was then removed, washed in distilled water, dried with alcohol and ether, and reexamined under the microscope. The change in its appearance is well shown by Fig. 2. The piece of lead was then replaced in the solution and, at frequent intervals, was removed in order that the change in the character of its surface might be observed under the microscope. The appearance of the same surface after an immersion of thirty-four days is shown in Fig. 3. The lack of

sharpness of definition in this photomicrograph is due to the fact that the surface was no longer plane, the solution having affected a greater transformation at some points of the surface than at others. These photomicrographs are of interest in connection with the photographs taken by Cohen¹ of the same phenomenon. While Cohen's photographs are natural size and hence do not reveal the rapidity with which the transformation into the gray modification of lead occurs, yet they bring out more satisfactorily than photomicrographs the extent of the disintegration.

Summary of Results.

(1) Five different types of lead electrode have been studied in a cell made up in the following manner:



Of these five electrodes the only one which proved to be constant and reproducible to within 0.3 millivolt was that in which the lead was deposited electrolytically on platinum.

(2) Freshly cast sticks of lead, after immersion for varying periods of time in an acidified solution of lead nitrate, lost their ductility and other properties commonly associated with lead. The gray mass thus obtained undoubtedly is an allotropic modification of the metal.

(3) Measurements of the electromotive force developed at 0° and 25° by cells in which freshly cast lead and the gray modification formed the electrodes and 0.2 N Pb(NO₃)₂ served as the electrolyte, failed to give any positive indication of a transition temperature.

(4) A calculation of the normal electrode potential of lead was made from the mean value of the electromotive force of cells involving a constant and reproducible lead electrode. The value of this potential was found to be 0.1318 volt at 25°.

(5) The electrodes were examined under the microscope and photomicrographs were made to show the rapidity with which freshly cast lead undergoes transformation when immersed in a solution of acidified lead nitrate.

HILLSIDE LABORATORY,
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY, No. 262.]

THE DISSOCIATION PRESSURES OF MERCUROUS CHLORIDE.

By ALEXANDER SMITH AND ROBERT PEYTON CALVERT.

Received February 14, 1916.

The vapor pressures of calomel, over limited ranges of temperature, have been studied by Wiedemann, Stelzner, and Niederschulte² and by

¹ *Trans. Faraday Soc.*, 10, 228 (1915).

² *Ber. deut. physik. Ges.*, 3, 159 (1905).

Smith and Menzies.¹ The pressures of vapor in equilibrium with the solid calomel were determined by the former for temperatures below 180° and by the latter for temperatures above 361°. In the one series, the highest pressure obtained was 0.5 mm.; in the other, the lowest pressure was more than 450 mm. For some work now nearing completion in this laboratory it is necessary to have data for certain points in the wide temperature interval not previously investigated. In this paper, that information is supplied. Since the entropy of vaporization is a more significant relation than is Trouton's rule, or any of the modifications of that rule which have been so extensively applied to vapor and dissociation pressures, the values of this constant for several dissociating substances have been calculated. We have included, also, a discussion of the various confining fluids which may be used in the static isoteniscope.

The Apparatus.—The measurements were made by use of the static isoteniscope and the apparatus previously described by the authors.² The isoteniscope was heated in a vigorously stirred bath of the molten nitrates of sodium and potassium. The temperature scale is that based on the ice point, steam point, and sulfur boiling point (taken as 444.7°); it could be reproduced, in successive calibrations of the platinum thermometer, to within $\pm 0.03^\circ$. The pressure readings are corrected to 0° and sea-level at latitude 45°.

Confining Fluids.—In any measurement with the static isoteniscope, the choice of a suitable material to confine the vapors is extremely important. In many cases alloys, or a pure metal, like bismuth, may be used, but they are of such high density that errors due to leveling may correspond to several tenths of a millimeter of mercury. The equimolar mixture of sodium and potassium nitrates is available at temperatures above its melting point, 222.4,³ and below 450° at which the liberation of oxygen becomes appreciable. The mixture gives a light, mobile, perfectly transparent liquid which can be leveled with precision. But, unfortunately, the hot nitrates act chemically on many vapors and thereby disturb the vapor pressure equilibrium. The eutectic of lithium and potassium chlorides⁴ gives, at high temperatures, a liquid having no appreciable vapor pressure and one which would seem admirably suited for confining the vapor of any chloride. But our experience has convinced us of the practical impossibility of using this mixture because, first, of its strongly hygroscopic nature and, secondly, of its attacking the glass, thus rendering the isoteniscope opaque.

The ideal material for confining a vapor is the liquid form of the sub-

¹ THIS JOURNAL, 32, 1541 (1910).

² Smith and Calvert, *Ibid.*, 36, 1363 (1914).

³ Harkins and Clark, *Ibid.*, 37, 1819 (1915).

⁴ Zemczuzng and Rambach, *Z. anorg. Chem.*, 65, 405 (1910).

stance whose vapor pressure is being determined. When the substance sublimes without melting, the temperature of melting can often be lowered below the boiling point, even for low pressures, by the addition of another salt. Thus, for confining the vapors of the chloride, the bromide and the iodide of ammonium, we have used the eutectic of the ammonium salt and the corresponding silver halide.¹ Also the eutectic of potassium chloride and the vaporizing substance has proved satisfactory in at least two vapor pressure measurements, the results of which are yet to be published.

In the work of Smith and Menzies on calomel,² the eutectic mixture of potassium and sodium nitrates was employed as confining liquid. Some interaction of the vapor with the nitrates occurred, causing a slow rise in pressure due to the accumulation of an excess of mercury vapor. The vapor was expelled and replaced by a fresh supply immediately before each reading. In the present work two different confining liquids were used in two series of measurements, namely, in the first, molten nitrates of sodium and potassium and, in the second, the eutectic of potassium chloride and silver chloride containing three mols of the former to seven of the latter and melting at 306°.³ With the mixture of chlorides, the rise in pressure, caused by the dissolving of the mercuric chloride in the confining liquid and the accumulation of an excess of mercury vapor, was very much slower than when nitrates were employed. By distilling the vapor through the confining liquid and practically saturating the latter with mercuric chloride before making an observation, the increase for a five-minute interval was reduced to less than one-tenth of that observed with the nitrates as confining liquid.

During this boiling-out process a very large deposit of mercury formed as a mirror in the upper cool part of the isoteniscope, thus affording another proof that calomel vapor dissociates giving free mercury.

TABLE I.—VAPOR PRESSURES OF CALOMEL—OBSERVATIONS.

Temp. °C.	P _{obs.}	ΔP.	P _{c.}
309.52*	105.1	+ 2.1	103.0
328.28	180.2	0.0	180.2
340.32*	259.1	+ 5.4	253.7
341.56	262.0	+ 0.6	261.4
354.57	372.3	+ 0.3	372.0
356.34*	399.1	+ 8.9	390.2
366.58	507.7	+ 0.1	507.6
367.72*	535.5	+13.0	522.5
375.10	621.3	+ 2.9	618.4
383.95*	781.4	+16.7	764.7

¹ Smith and Calvert, *Loc. cit.*

² *Loc. cit.*

³ Zemczuzng, *Z. anorg. Chem.*, 57, 275 (1908).

The Observations.—The pressures were read five minutes after the boiling out had been stopped ($P_{\text{obs.}}$) and again five minutes later. The difference (ΔP), when subtracted from $P_{\text{obs.}}$, gives the pressure (P_0) corrected to the time zero at which the boiling out ceased. The results are also shown graphically in Fig. 1.

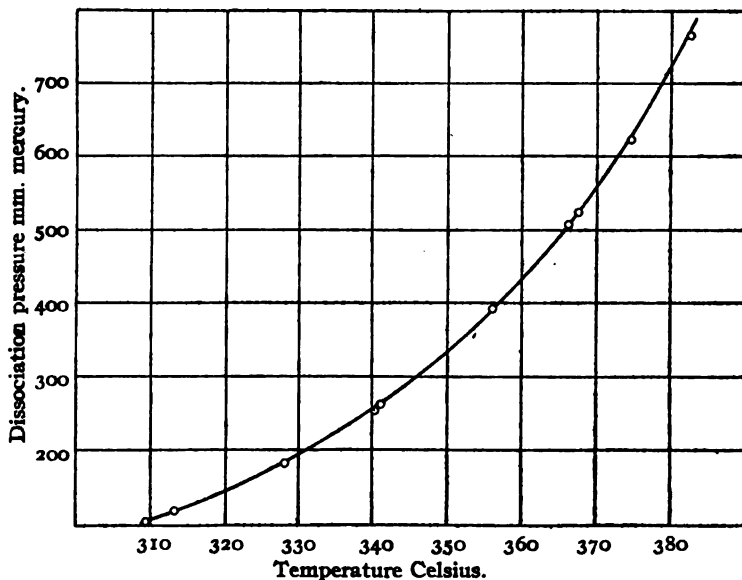


Fig. 1.

An asterisk indicates that the observation was made with the molten nitrates as confining fluid in the bend of the isoteniscope. Much more weight is to be given to the results obtained by the use of the chlorides

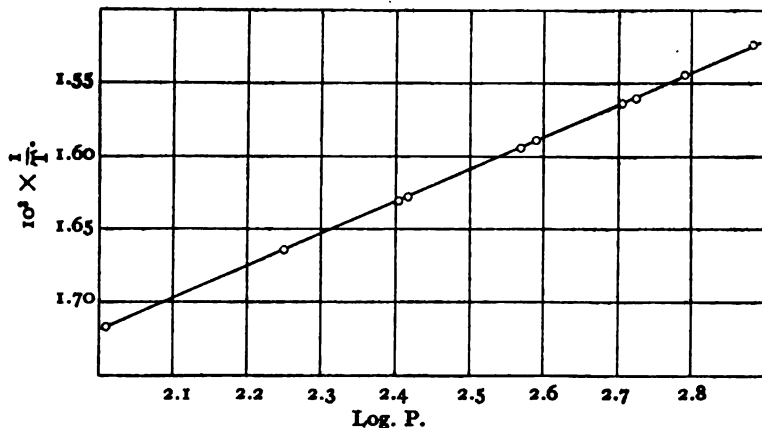


Fig. 2.

for the confining liquid; yet it will be observed that Fig. 2, in which $\log P$ is plotted against $1/T$, that the final data for both series gives points lying closely along the same straight line. This has especial interest in view of the fact that the correction applied for the increase in pressure with time was very large in the one series and almost negligible in the other.

Kirchoff-Rankin-Dupre Equation.—For the purpose of interpolation and for testing the accuracy of our readings, we have derived an equation of the Kirchoff-Rankin-Dupré type.

$$\log p = -\frac{7792.10}{T} - 12.2309 \log T + 49.2048.$$

From this we have calculated the following dissociation pressures of calomel, in mm. of mercury, for even temperatures:

TABLE II.—DISSOCIATION PRESSURES OF CALOMEL AT EVEN TEMPERATURES.

Degree.	Mm.	Degree.	Mm.	Degree.	Mm.
300	74.4	340	251.4	380	696.8
310	103.0	350	329.9	383.7	760.0
320	140.5	360	428.0
330	189.2	370	548.9

The "boiling point," at 760 mm., is 383.7°. Harris and Meyer found 357°;¹ Jonker, 373°;² and Smith and Menzies, 382.5°.³

Although the solution of the above equation for the vapor pressure at any given temperature is quite easy, the calculation of the temperature corresponding to a given pressure is more troublesome. Now, in these measurements the chief errors lay in the temperature control and measurement and not in the reading of the pressure. Consequently, in testing the consistency of the result, it is preferable to express the deviations of the individual observations from the mathematical curves, represented by the Kirchoff-Rankin-Dupré equation, in degrees rather than in mm. Table III gives, for each pressure, the temperature observed

TABLE III.—DISSOCIATION PRESSURES OF CALOMEL.

Pressure.	Temp. (obs.).	Temp. (calc.).	Δ .
103.0	309.52*	309.98	+0.46°
180.2	328.28	328.34	+0.06°
253.7	340.32*	340.33	+0.01°
261.4	341.56	341.38	—0.18
372.0	354.57	354.56	—0.01
390.2	356.34*	356.40	+0.06
507.6	366.58	366.84	+0.26
522.5	367.72*	367.98	+0.26
618.4	375.10	374.94	—0.16
764.7	383.95	383.98	+0.05

¹ Ber., 27, 1484 (1894).

² Chem. Weekblad, 6, 1035 (1909).

³ Loc. cit.

and the temperature calculated by means of the formula and the difference (Δ) between the two values. The arithmetical mean of these deviations is 0.15° which, divided by the square root of the number of observations, *i. e.*, by 3, gives $\pm 0.05^\circ$ as indicative of the precision of the measurements.

The Entropy of Vaporization.—Hildebrand¹ has pointed out that Trouton's rule, namely, that the ratio of the heat of vaporization to the boiling point of the absolute scale is a constant, or, as he states it, that the entropy of vaporization to one atmosphere pressure, is constant, does not hold even for normal substances, especially at extreme temperatures. The constants increase as the boiling points are higher. He points out that for normal liquids entropy of vaporization to a fixed molecular concentration of each vapor is more nearly constant.

For any vapor, at pressures so low that the laws of gases are applicable, $p = RTc$, where c is the molecular concentration. Hence, $\log p = \log T + \log Rc$. When c is 0.00507 mol per liter, $\log Rc = -0.5$. Now, $d \log p / d \log T = L/RT$. For the purpose of comparison with Hildebrand's results, we have calculated the value of the entropy of vaporization L/RT_c when $\log p = \log T - 0.5$. Following him, we have also calculated the value of L/RT_p , where the vapor pressure is 100 mm., since at this lower pressure Trouton's rule should give more constant values than at 760 mm. The values at 760 mm. are given as well.

TABLE IV.—ENTROPY OF VAPORIZATION TO FIXED MOLAR CONC. ($c = 0.00507$).

Substance.	L/RT_c where $\log p = \log T - 0.5$.	L/RT_p where $\log p = 2.00$.	L/RT_p where $p = 760$ mm.	T_c $c = 0.00507$.	T_p $p = 100$ mm.	T_p $p = 760$ mm.
PH ₃ I.....	20.7	20.5	17.6	301.5°	302.2°	335.6°
PCl ₃	19.8	20.7	16.8	395	390	435.8
N(CH ₃) ₃ Cl.....	17.5	16.4	25.4	469	450	506.3
N(CH ₃) ₃ I.....	18.7	18.7	18.7	534	519	578.5
NH ₃ Cl.....	17.5	17.9	16.9	562	544	610.8
Hg ₂ Cl ₂	17.7	18.7	14.9	604	582	656.7
NH ₄ Br.....	17.2	18.0	16.3	616	593	667.6
NH ₄ I.....	18.2	20.1	15.9	627	605	677.9
Normal liqs.....	13.1-13.9	11-15.1
Assoc. liqs.....	16.0-16.7

For the purpose of comparison, the corresponding values, as given by Hildebrand for normal and for associated liquids, are indicated. In the case of dissociating substances, such as our table contains, it was to be expected that the heats of vaporization (including heats of dissociation) would be higher. It should be noted that our values refer to a constant

¹ THIS JOURNAL, 37, 970 (1915).

total molecular concentration both of the undissociated molecules and of the molecules of the products of the dissociation.

Summary.

The dissociation pressures of calomel for temperatures between 309° and 384° are given. The pressure, 760 mm., is reached at 383.7° .

The Kirchoff-Rankin-Dupré equation represents the results satisfactorily.

The entropies of vaporization to constant molecular concentration for eight dissociating substances are recorded.

Confining liquids are discussed.

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION,
WASHINGTON, D. C.]

THE OXIDES OF IRON. I. SOLID SOLUTION IN THE SYSTEM $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ ¹.

BY R. B. SOSMAN AND J. C. HOSTETTER.

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CONTENTS.—Introduction. State of Knowledge of the Oxides of Iron. Apparatus Employed. Materials: Ferric Oxide; Merck's "Reagent Iron Oxide;" Oxide from Electrolytic Iron; Sibley Ore; Magnetite; Oxygen. Special Problems: Optical Properties of the Oxides of Iron; Reduction of Iron Oxides by Platinum; Disappearance of Oxygen in Furnace; Adsorption of Gases. Questions of Equilibrium: Reproducibility of Dissociation Pressures; Accuracy of Temperature and Pressure; Pressures from Ferric Oxide from Different Sources; Effect of Temperature Gradient in Furnace; Comparison of Rising and Falling Temperatures; Pressures Obtained by Oxidation of Magnetite. The System $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$: Experimental Results: General Plan; Methods of Analysis; Total Iron; Pressure-composition Isotherm at 1200° ; Pressure-composition Isotherm at 1100° ; Form of Dissociation-pressure Curve near Fe_3O_4 ; Optical Properties. Comparison with Previous Investigations. Summary.

Introduction.

The silicate systems which have hitherto been the subjects of study in this laboratory have all been made up of oxides which are apparently unaffected by atmospheric oxygen at temperatures below 1600° . They could therefore be melted in platinum-wound furnaces in the open air. The oxides which can be so treated include silica, alumina, magnesia, lime, and the alkalis. But iron, which is one of the most important constituents of natural silicates, changes its form of combination and the properties of its compounds according to the amount of oxygen which is combined with it, and, furthermore, the amount of oxygen so combined is constantly changing, especially at high temperatures. It becomes necessary, then, to take account of oxygen as one of the components in any silicate system containing iron.

¹ Presented in abstract at the Seattle Meeting of the American Chemical Society, Sept. 1, 1915.

Early in the work on the iron-bearing silicates, it became evident that we must know something about the dissociation pressures and chemical relationships of the iron oxides, in order to explain complications arising in the silicate systems. We found the published information too incomplete for our purpose, and have therefore devoted some time to the study of the system iron-oxygen.

This paper will deal with the equilibrium conditions that must be met in the study of the dissociation of Fe_2O_3 , and with the information obtained on the series Fe_2O_3 - Fe_3O_4 by measurement of the dissociation pressures, that is, the oxygen pressures in equilibrium with the oxides.

State of Knowledge of the Oxides of Iron.

Three principal (anhydrous) oxides of iron have long been familiar in chemical literature: ferric oxide, Fe_2O_3 , occurring in nature as the mineral hematite; ferroso-ferric oxide, Fe_3O_4 , occurring as magnetite; and ferrous oxide, FeO , which is not known to occur in nature. A less common mineral form is martite, which has a somewhat variable composition intermediate between Fe_2O_3 and Fe_3O_4 . It is commonly described as "hematite pseudomorph after magnetite," as it usually lies nearer hematite than magnetite in composition, but has the external octahedral form of magnetite. In addition to these natural oxides, many other oxides have been prepared and described by various investigators. Some of these are listed below in the order of their oxygen content (Table I).

It would be too long a task to review completely the history of the many researches upon the iron oxides. It must suffice for the present to say that as most of these have been conducted at ordinary temperatures and in connection with water solutions, with attending complications in the formation of colloidal hydroxides, they have not yielded the information necessary to an understanding of the equilibrium relationships in silicate mixtures at higher temperatures. Some of the investigations on dissociation pressures of the iron oxides will be discussed in connection with our own conclusions later in this paper.

TABLE I.
Principal Oxides of Iron Described in Chemical Literature.

Formula.	Described by	Percentage of the iron which is in the ferrous state.
Fe_2O_3 , hematite		0.00
Fe_7O_{10} or $(\text{FeO})_3(\text{Fe}_2\text{O}_3)_2$	Kohlmeyer	14.29
$\text{Fe}_{12}\text{O}_{18}$ or $3(\text{FeO})_2(\text{Fe}_2\text{O}_3)_3$	Kohlmeyer	23.08
Fe_9O_{11} or $2(\text{FeO})_3(\text{Fe}_2\text{O}_3)_2$	Haber and Kaufmann	25.00
$\text{Fe}_{11}\text{O}_{15}$ or $3(\text{FeO})_4(\text{Fe}_2\text{O}_3)_2$	Kohlmeyer	27.27
Fe_3O_4 or $(\text{FeO})(\text{Fe}_2\text{O}_3)$, magnetite		33.33
Fe_4O_5 or $2(\text{FeO})(\text{Fe}_2\text{O}_3)$	Gregory	50.00
Fe_5O_6 or $3(\text{FeO})(\text{Fe}_2\text{O}_3)$	Döbereiner	60.00
Fe_6O_7 or $4(\text{FeO})(\text{Fe}_2\text{O}_3)$	Hauser	66.67
FeO		100.00

An alternating current at low voltage is sent through the furnace tube, which is made of an alloy of 80 parts platinum and 20 rhodium.¹ The tube is 15 mm. inside diameter and 200 mm. long, with walls 1 mm. thick. The current is carried in by water-cooled terminals; the upper terminal is fixed to the furnace jacket, while the lower terminal moves with the expansion and contraction of the furnace tube. The cooling water is led into the lower terminal by lead pipes, and the current is carried by a sheaf of flexible copper strips. The lower leads are insulated from the furnace jacket by the stone base of the jacket, and are prevented from accidentally touching the walls by mica sheets around the inside of the jacket.

The lower end of the platinrhodium tube is extended by a steel tube, capped with a screw cap and sealed with kolloid.² The upper end is likewise extended by a steel tube into which a glass tube is sealed.

Branches from the glass tube connect with the Gaede molecular vacuum pump, on the one hand, and with the pressure gages on the other. The interior of the furnace and gages is kept dry by a tube of P_2O_5 in the bottom of the steel extension of the furnace tube.

The charges are contained in a small platinum crucible suspended by two platinum wires sealed into a glass cap, which is attached to a ground glass conical joint at the top of the tube above the furnace. The two wires of the platinum-platinrhodium thermoelement are also sealed through this glass cap, and the four wires are insulated from one another by transparent fused silica or Marquardt porcelain capillaries. The two suspension wires may also be used as the leads for the determination of melting points, *et cetera*, by the quenching method.

There are three pressure gages: (1) a McLeod vacuum gage of 500 cc. capacity from Leybold (shown at M_1); (2) a similar gage of 50 cc. capacity made here (M_2); (3) a mercury manometer read to 0.01 mm. by means of parallel knife edges and a vernier. The latter is the manometer used in previous work on the nitrogen thermometer.³ It has an excellent scale, calibrated throughout its length to 0.01 mm. by the Normal-Aichungs-Kommission in Charlottenburg. The three gages, compared against one another at various pressures within their ranges, agreed within the error of their readings. We have in this combination of gages a range of pressure measurement from 0.000001 mm. mercury up to about 2.5 atmospheres.

¹ The tube was made by Dr. Heraeus of Hanau, to whom we have several times had occasion to express our indebtedness for his interest in the forwarding of high-temperature investigations.

² A Canada balsam substitute of constant "melting point" and low vapor pressure, made by Voigt & Hochgesang.

³ Day and Clement, *Am. J. Sci.*, [4] 26, 415 (1908); *Publ. Carnegie Inst. Washington*, No. 157, p. 19.

The furnace jacket is an inverted iron pot, closed at the bottom by a disk of Alberene stone through which pass (1) the two conductors in parallel which carry the current to the lower end of the platinrhodium tube, together with the tubes for the cooling water, and (2) the steel extension of the platinrhodium tube. The latter is surrounded by a water-jacketed steel tube and cap.

The jacket is evacuated independently of the inside vacuum by means of a May-Nelson pump. There is no connection between the inside high vacuum and the outside "ordinary" vacuum. No insulation or refractory material is used excepting a magnesia tube surrounding the platinrhodium tube. The outside vacuum removes any danger of collapsing the hot furnace tube at high temperatures, and also provides an efficient heat insulation. The furnace jacket is cooled by a coil of lead pipe on the outside carrying cold water. An observation window permits optical temperature measurements to be made from without.

The current is supplied to the furnace from the secondary of a small 25 : 1 transformer. The primary of the transformer is supplied by a motor generator of 60 cycles and a voltage range from 0 to about 300 volts. The generator voltage is regulated by means of its field current, which is supplied by a 110 volt storage battery and passes through rheostats alongside the potentiometer. By regulation of the field current the furnace current can be regulated without any waste of electrical energy, and if the voltage applied to the motor of the motor generator is reasonably constant, the temperature can be held constant without difficulty to one degree at 1500°. This degree of constancy is very often necessary for accurate measurements of the dissociation pressures of iron oxides, as these pressures change quite rapidly with temperature.

Materials.

Ferric Oxide.—Ferric oxide is rather difficult to prepare pure, and not many preparations of the required purity can be found on the market. We have used several different preparations in the course of the work.

Kahlbaum's "Eisenoxyd zur Analyse mit Garantieschein" is said by the manufacturer to contain 99.60% Fe_2O_3 , 0.40% moisture, no manganese and no alkalis. Its color is between raisin-black and dark slate-purple, 65''' l, of Ridgway's color system.¹ Our analysis of this oxide gives: Fe_2O_3 , 99.70; FeO , 0.09; SiO_2 , 0.01; Na_2O , 0.04; TiO_2 , less than 0.01; MnO , less than 0.01; P_2O_5 , less than 0.005; water-soluble, 0.02; total, 99.85. The remainder of 0.15% may be moisture.

Merck's "Reagent Iron Oxide."—No analysis is given by the manufacturer. It is stated in the catalog that this oxide is made according to the method of Brandt (ignition of nitrate made from pure iron).² Ac-

¹ Robert Ridgway, "Color Standards and Color Nomenclature," 1912.

² L. Brandt, *Chem. Ztg.*, 32, 812, 830, 840, 851 (1908).

cording to the tests which it is supposed to pass, this oxide should contain, at the most: 0.1% water and volatile substances, 0.01 water-soluble substances, 0.005 Cl, 0.0032 N_2O_5 , 0.035 SO_3 , 0.033 SiO_2 , 0.003 FeO, 0.01 substances insoluble in HCl, 0.02 Al_2O_3 , 0.007 Ca, 0.0002 Mg. Its color is quite different from that of Kahlbaum's oxide, and is between Prussian-red and ocher-red 5" l. Our analysis of Merck's oxide gives: Fe_2O_3 , 99.30; FeO, 0.07; SiO_2 , 0.01; Na_2O , 0.05 (as Na_2SO_4 , 0.11); MnO, less than 0.01; TiO_2 , less than 0.01; P_2O_5 , less than 0.005; water-soluble, 0.02; H_2O at 100°, 0.34; H_2O (and adsorbed gases?) lost in vacuum at 500°, 0.50. Total, 99.82 to 99.98.

Oxide from Electrolytic Iron.—Pure electrolytic iron made about 1907, by C. F. Burgess,¹ was dissolved in nitric acid (J. T. Baker's C. P.), filtered, evaporated to form the basic nitrate, and ignited in small portions over the blast lamp in a platinum crucible. No analysis was made of the product. The original metal contains no manganese and only traces of sulfur, phosphorus, and silicon.

Sibley Ore.—This is one of the purest natural ferric oxides available in large quantity, although, of course, selected hematite crystals are much purer. It is standard sample No. 27 of the Bureau of Standards, and contains, according to the Bureau's certificate and its Circular No. 26: 69.2% total iron, 0.036% phosphorus, 0.78% SiO_2 , no Mn and no Ti. Ferrous iron does not seem to have been looked for in the analyses which have been published, but we find a surprisingly large percentage of FeO in this sample. Four analyses, on two different bottles, gave 2.27, 2.24, 2.34 and 2.25%; mean 2.28%. On the basis of 69.2% total iron, as reported by the Bureau, the calculated composition in terms of oxides is: 96.41 Fe_2O_3 , 2.28 FeO, 0.78 SiO_2 , 0.09 P_2O_5 , 0.01 V_2O_5 ;² total, 99.57.

Magnetite.—Probably the purest and best crystallized magnetite ever obtained in large quantity was from the "Lovers' Pit" of the Barton Hill mines at Mineville, N. Y. We collected a number of specimens from this mine in 1914. The sample (No. 3g) used for the present work consisted of clean crystals from a pillar in the Lovers' Pit, taken about 3 ft. below the hanging wall or 10 ft. above the foot wall.³ This magnetite contains by our analysis 30.72% FeO, 72.08% total iron, and 0.01% moisture coming off at 100°. It therefore contains 99.00% pure Fe_3O_4 ,

¹ For this we are indebted to Professor C. F. Burgess, of the University of Wisconsin.

² Cain and Hostetter, *J. Ind. Eng. Chem.*, 4, 254 (1912). *Bur. Standards Tech. Paper*, No. 8.

³ We are greatly indebted to Mr. Rigby and the officials of Witherbee, Sherman & Co., for assistance in collecting a series of magnetite specimens, concerning which we hope to report more in detail at a later date.

0.63% excess Fe_2O_3 , and 0.37% impurities. This 0.37% consists chiefly of insoluble quartz.

Oxygen.—Oxygen was made from sodium peroxide, dried and passed over copper oxide in a resistance furnace heated to 650° to oxidize any hydrogen that might be present, again dried over CaCl_2 and P_2O_5 and stored over mercury. For use it was drawn out through another P_2O_5 tube. Its purity is shown by the fact that less than 0.01% remained unabsorbed by magnetite when the amount of oxygen was insufficient to completely oxidize the magnetite to Fe_2O_3 .

Special Problems.

Optical Properties of the Oxides of Iron.—A few of the difficulties peculiar to the study of the iron oxides deserve mention. The first of these is the opacity of the oxides. In the study of the silicates the microscope is an almost indispensable tool; by its aid one can tell at once how many and what phases are present in a given preparation. But in the present work we have had to fall back upon the chemical analysis of each charge in order to secure the information that the microscope would have yielded if the oxides had possessed easily measurable optical properties. This feature has made the work much slower than it would otherwise have been.

By the use of his immersion glass of selenium and tellurium, Dr. H. E. Merwin, of this Laboratory, has, however, succeeded in contributing a great deal of assistance. It is possible by these means to get some light through the oxides of compositions lying between pure Fe_2O_3 and a point midway in composition between Fe_2O_3 and Fe_3O_4 ; the refractive indices and double refraction can then be determined. His detailed results will be presented later in the paper.

Reduction of Iron Oxides by Platinum.—Another difficulty peculiar to the study of the iron oxides is their reduction by platinum. The charges were heated in small platinum crucibles 18 mm. deep and 8 to 10 mm. in diameter. These crucibles almost always gained in weight from 0.1 to 1.0 mg. during a series of measurements. As we have already shown in a recent publication,¹ this gain in weight is due partly to iron reduced by the platinum and taken up in solid solution. The rest of the gain in weight consists of rhodium and platinum from the furnace tube.

Platinum acts on both hematite and magnetite at 1200° under low pressures of oxygen, absorbing iron and giving off oxygen. It also reacts with magnetite in the same way at 1600° and at the usual atmospheric pressure of oxygen. On the other hand, it is well known to analysts

¹ Sosman and Hostetter, "Reduction of Iron Oxides by Platinum with a Note on the Magnetic Susceptibility of Iron-bearing Platinum," *J. Wash. Acad. Sci.*, 5, 293-303 (1915).

that platinum crucibles in which Fe_2O_3 is ignited in air for weighing in analytical procedures take up no such amounts of iron as we have found taken up under the above-mentioned conditions. The reason for these differences of behavior is apparent from the relations of iron and platinum in their alloys, as interpreted by the phase rule.

The system contains 3 components: platinum, iron, and oxygen. Iron and platinum form a continuous series of solid solutions.¹ The oxidation of the iron causes it to separate from the platinum as an oxide. If we now have present the three phases, iron-platinum alloy, solid oxide, and gaseous oxygen, and assume a certain concentration of iron in the platinum (say 0.01%), and a certain temperature (say 1200°) then there must be a definite oxygen pressure in equilibrium with this system. If the existing pressure of oxygen is less than this equilibrium pressure, the oxide will dissociate and metallic iron will be absorbed by the platinum. If the pressure of oxygen be greater, on the other hand, iron from the platinum solution will be oxidized, the oxide will separate on the surface of the metal, and the concentration of the iron in the platinum will be reduced.

It is evident from the fact that melted magnetite is reduced by platinum in air that at 1600° the oxygen pressure of the air (about 152 mm.) is less than the oxygen pressure in equilibrium with dilute solutions of iron in platinum. Similarly, at 1200°, it is found that 18 mm. oxygen is less than the equilibrium oxygen pressure, and at this temperature and pressure iron is absorbed by platinum from all oxides between Fe_2O_3 and Fe_3O_4 . 152 mm. oxygen, however, is greater than the oxygen pressure of any but the most extremely dilute solution of iron in platinum at 1200°, and at this temperature, which is seldom exceeded in igniting iron oxide precipitates for analysis, there is no appreciable reduction of Fe_2O_3 by platinum in the open air.²

These considerations explain the very common occurrence of small amounts of iron in platinum, since platinum will exercise its reducing action on any material containing iron oxides with which it comes in contact, provided that the temperature is above, say, 1000°. At lower temperatures, on the other hand, and with abundant access of atmospheric oxygen, no appreciable reduction is to be expected.

Disappearance of Oxygen in Furnace.—In many of the measurements a gradual decrease of pressure was observed at 1200° and higher, and a calculation of the final composition of the charge, from the original composition and from the amount of oxygen removed, showed that more

¹ Isaac and Tammann, *Z. anorg. Chem.*, 55, 63-71 (1907).

² This kind of contamination of platinum by iron is to be distinguished from the contamination caused by the reducing action of incompletely burned gases during the ignition of ferric oxide over a gas flame.

ferric and less ferrous iron should be present than was actually obtained by analysis. A series of measurements made with oxygen alone showed that oxygen was in fact disappearing at the higher temperatures. No change occurred at 500° or lower, showing that the loss was not due to ordinary leakage. On the other hand, a very small, although measurable and apparently constant evolution of gas was observed at 1450° when the furnace was completely evacuated; this evolution seemed to be unaffected, however, when the pressure in the "outside vacuum" was allowed to rise. A possible explanation of these phenomena is that when the furnace is heated to a high temperature the silver-soldered joint between platinum and steel is warmed sufficiently to allow the diffusion of oxygen through the silver, which is known to occur at a relatively low temperature. It has not been possible as yet to prove this explanation. As the rate of disappearance of oxygen is too small to affect appreciably the results reported in this article, this source of loss has been neglected for the present.

Adsorption of Gases.—The pressure within the vacuum apparatus always rises slowly on standing. We have ascribed this to the slow escape of gases from the surface of the glass. As the apparatus must be opened to the air for the insertion and removal of oxide charges, there is abundant opportunity for oxygen or other gases to be taken up by the glass.

On one occasion the apparatus stood unused for 27 days, and there was opportunity to observe the slow rise of pressure due presumably to gases from the glass. The measurements are plotted in Fig. 2. After

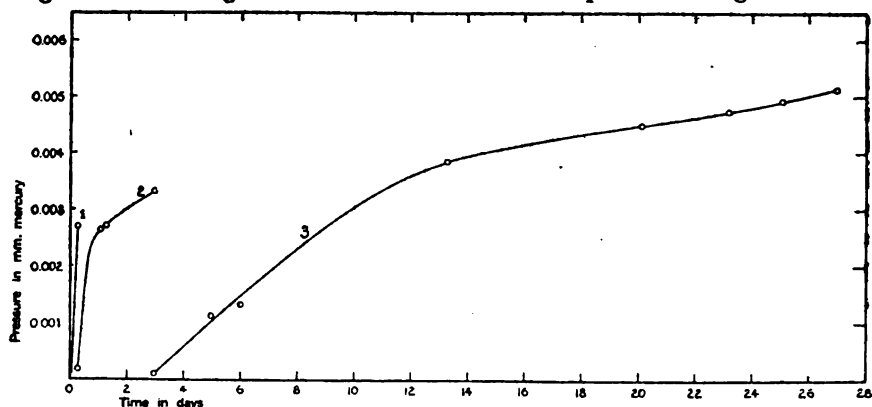


Fig. 2.—Evolution of gases from walls of apparatus.

the initial pumping the pressure rose in 11 minutes from 0.00060 mm. to 0.00270 mm. (Curve 1). It was immediately pumped out a second time, after which the pressure rose in 2 days and 17 hours from 0.00016 mm. to 0.00332 mm. (Curve 2). This gas was then pumped out, following which the pressure rose still more slowly, taking 24 days to rise from

0.00010 mm. to 0.00515 mm. (Curve 3). The mercury cut-off (C in Fig. 1) was closed during the entire time, so that no gas could have been furnished by stopcock grease.¹

Some gas may also be held on the surface of the platinum tube. A small amount was always obtained when the furnace was heated without a crucible or charge in position. It is possible, however, that some of this comes from minute amounts of Fe_2O_3 which has been blown out of crucibles or which may even have been volatilized and deposited on the furnace walls on cooling. The amounts of gas in question were too small to have an appreciable effect on the pressures reported in this article.

Questions of Equilibrium.

Reproducibility of Dissociation Pressures.—Before it can be assumed that a given experimental procedure is yielding results that represent conditions of true chemical equilibrium, there are several questions to be answered experimentally. The first of these concerns the reproducibility of the pressures under given experimental conditions. In general, we have found that, using equal weights of the same initial oxide, we obtained at a given temperature pressures which in most cases agreed within the limits of error. In some cases, however, the pressures differed by amounts considerably larger than the errors of reading temperature and pressure, especially in the case of Merck's oxide. These results will be specifically discussed later. An example of the reproducibility of pressure measurements made under similar conditions is to be found in the second, third, fourth and fifth measurements in Table II.

Accuracy of Temperature and Pressure.—The temperature can be regarded as certain within 2° , since calibrations by the thermal curve method, with a charge of diopside ($\text{MgSiO}_3\cdot\text{CaSiO}_3$) in place of the iron oxide charge, gave 1389.4° and 1390.3° , as against 1391.2° , the original nitrogen thermometer value. The degree of accuracy of the pressure measurements varies widely, according to the degree of compression on the McLeod gages and the magnitude of the pressure. 1 mm. on the large McLeod gage corresponds to 0.0004 mm. in 0.1500 mm. at the lowest compression, or to 0.000004 mm. in 0.000100 mm. at the highest compression. Pressures above 3.00 mm. were read directly, with an accuracy of 0.02 mm.

Pumping for different lengths of time before heating had no considerable effect on the pressures. Holding the temperature constant produced a gradual change, and yielded a constant value in from 10 to 20 minutes, if the effects of by-reactions (reduction by platinum and absorption of oxygen) were taken into account.

¹ At this time the cap which carried the thermoelement wires was sealed to the furnace tube with kolloidith.

Pressures from Ferric Oxide from Different Sources.—Preliminary tests showed that oxide from different sources gave pressures of the same order, when equal amounts were heated at the same temperature, but that there were some differences considerably larger than could be accounted for experimentally. Later measurements showed rather unsatisfactory results for Merck's oxide, which gave at 1200° , on 0.5 and 1.0 g. samples, pressures of from 1.39 to 1.95 mm., a rather large variation for which no cause is known. Kahlbaum's oxide gave 2.07 mm., a slightly higher pressure than Merck's highest, but still somewhat lower than that obtained by oxidation of magnetite. Pure ferric oxide, on the other hand, made from nitrate from electrolytic iron, and heated in oxygen at 1200° , gave pressures in exact agreement with those obtained by the oxidation of magnetite. Natural hematite ore (Sibley), and pure oxide from nitrate ignited in air, gave pressures differing by only 0.02 mm., but were not directly compared with the other oxides.

In general, therefore, it may be said that the oxides from different sources are in fairly good agreement, with the exception of Merck's, which is rather low and variable. Measurements on products which have not been ignited are subject to uncertainties from the presence of moisture and adsorbed gases of all kinds, and further work would be necessary to completely explain these variations in the commercial products.

Effect of Temperature Gradient in Furnace.—Shortly after the preliminary experiments, a series of tests was made to determine the effect of temperature gradient in the furnace. The uniformity of temperature could not well be tested by direct measurement, as a complicated arrangement of apparatus would have been necessary to permit of moving the thermoelement up and down in the completely sealed furnace. An equally sensitive test was made, however, by taking a series of measurements of the oxygen pressures produced by 0.5 g. charges of Merck's ferric oxide, heated under exactly similar conditions as to rate and time of heating but at various levels in the furnace. In our preliminary measurements of dissociation pressures the thermoelement junction was always placed 3 to 5 mm. above the top of the charge of oxide, so that the change in weight of the charge could be determined without uncertainty due to oxide adhering to the wires. It is obvious that near the top of the furnace the thermoelement, under these conditions, will be colder than the bottom of the charge, whereas near the bottom of the furnace the reverse will be true. Hence if the temperature of the thermoelement is set to the same value in both positions, the temperature of the charge, and therefore the pressure obtained, will be greater near the top than near the bottom of the furnace. If two or more pressures obtained near the middle of the furnace agree within the range of reproducibility of these pressures proof is afforded that there is a space of uniform tem-

perature equal to the distance between the highest position of the thermoelement and the lowest position of the bottom of the charge. Measurements can therefore be made on charges set in this part of the furnace with the assurance that the temperature of the charge is uniform and is represented accurately by the temperature of the thermoelement. This condition is further assured by packing deep charges into the crucible with a polished steel plunger which shapes the surface in such a way that there is a central well, in which the thermoelement is inserted, so that it is actually within, but not in contact with, the charge.

The result of the uniformity tests is shown in Table II. The distance from the top of the furnace tube to the top of the crucible in millimeters is given in the third column, and the pressure in millimeters of mercury in the fourth column. The degree of reproducibility of the pressures is shown by the second, third fourth and fifth measurements. The pressures at depths of 85, 92 and 95 mm. are practically constant. Since the depth of the crucible is 18 mm. there seems therefore to be a range of about 25-30 mm. in which the temperature is uniform within one degree, judging from the variation of pressure, which is of the order of magnitude of 0.01 mm. per degree under the conditions of the tests. For subsequent measurements the crucible was always placed in the middle of this zone, and the thermoelement brought near the center of gravity of the charge as explained above. The charges varied in depth from 5 to 10 mm.

TABLE II.

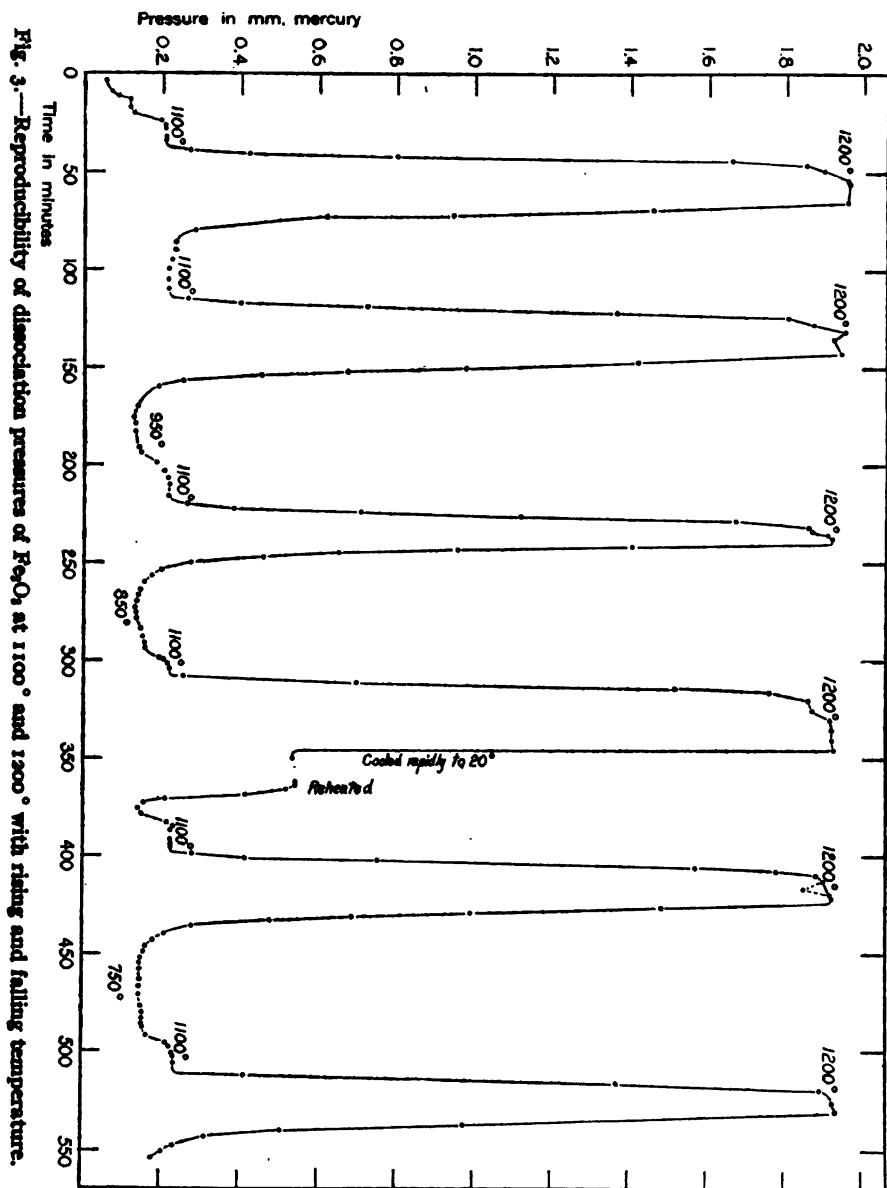
Temperature Distribution in Furnace, as Indicated by Pressures Obtained at Various Levels at 1100°.

No.	Weight oxide. Mg.	Distance from top. Mm.	Pressure. Mm.
1345	493.3	65	0.610
1347	502.9	75	0.330
1349	504.0	75	0.305
1351	502.9	75	0.320
1355	503.8	75	0.315
1358	501.8	85	0.215
1362	501.6	92	0.210
1360	507.1	95	0.195
1361	499.6	107	0.120

Comparison of Rising and Falling Temperatures.—True equilibrium can be assured only if the same pressure is obtained both by the addition and by the removal of oxygen. One method of changing the amount of oxygen in the charge is to change the temperature. If it is raised, oxygen is removed from, if lowered, oxygen is added to, the charge. If the temperature is then brought back to its original value, the same pressure should be obtained as before.

The results of a series of tests with Merck's oxide are presented in Fig. 3, and show that, on the same charge of oxide, substantially the

same pressures are obtained at 1100° with rising and with falling temperatures. The pressures at 1100° and 1200° are also shown to be uninfluenced by heating the charge at 750° , 850° , or 950° . The unab-



sorbed or slowly absorbing residue of 0.15 mm. which appears at 750° and 850° probably represents in part nitrogen or air adsorbed in the finely powdered oxide; the rapid drop to lower temperatures from 1200° also

leaves part of the original oxygen of the oxide unabsorbed, because of the slowness of diffusion and reaction at the lower temperatures.

Pressures Obtained by Oxidation of Magnetite.—A second method of comparing the effects of adding and removing oxygen is to use Fe_3O_4 as the initial solid, and add various amounts of oxygen, comparing the pressures at a given temperature with those obtained by starting with Fe_2O_3 .

The results obtained with pure Fe_2O_3 made from Burgess electrolytic iron through the nitrate, and heated beforehand in a current of oxygen at 1200° , are in exact agreement with the pressures of oxidized magnetite, as is evident from Fig. 5. In addition to the single points, one series was run in which oxygen was added in excess at the start, and then withdrawn in steps as in the case of oxidized magnetite. These results also are in excellent agreement with the oxidized magnetite.

The pressures obtained by heating Kahlbaum's and Merck's Fe_2O_3 are somewhat lower than the pressures, at a corresponding composition of the solid, obtained by oxidizing magnetite. Nevertheless, each gives every appearance of being in equilibrium. The pressure from Merck's oxide, as shown in Fig. 3, returns repeatedly to the same value after heating at various lower temperatures. The magnetite, in the course of being heated up to 1200° , was sometimes held at 1100° until completely oxidized to the composition of Fe_3O_4 , yet the pressures obtained on further heating and dissociating the oxide so formed were no lower than those obtained by heating directly to 1200° .

Whatever may be the cause of the low results obtained with Merck and Kahlbaum oxides, it is not evident in the optical properties of the products, for the crystals not only appear optically as a single phase, but the product formed by oxidation of magnetite has the same optical properties as the pure artificial oxides, and also the same as pure natural hematite.

The System Fe_2O_3 – Fe_3O_4 : Experimental Results.

General Plan.—In general, our preliminary measurements showed clearly that the oxygen pressure depends not only upon the temperature, but also upon the weight of the charge and the volume of the gas space—in other words, upon the composition of the charge of oxide at the time of measurement. This can have only one meaning, namely, solid solution between the original Fe_2O_3 and some lower oxide.

The existence of a solid solution series is best demonstrated by a pressure-composition isotherm. The temperature of 1200° seemed most favorable for our purpose. On the one hand, the pressures obtained are high enough so that the by-reactions (page 813) are of small effect; on the other, the pressures are not so high that the amount of oxygen in the gas space forms too large a proportion of the oxygen in the charge.

For our final series, we preferred to start with magnetite and add oxygen, for the following reasons: Ferric oxide, Fe_2O_3 , always contains some moisture and adsorbed gas, which cannot be removed by pumping alone; the charge must be heated to a high temperature in order to drive them off. This heating dissociates the oxide, so that it must be reoxidized by slow cooling, and also sinters it into a solid cake, so that the initial conditions of the charge are rendered uncertain. Magnetite, on the other hand, can be heated up for a few minutes initially, cooled, and the residual adsorbed gas pumped out. Its own dissociation pressure is so very low that its composition is not changed to any measurable extent by this treatment, and the charge is furthermore not sintered.

The procedure was as follows: The apparatus was first evacuated to 0.001 mm. or lower. The mercury cut-off C was closed, and the charge was heated to 1200° for a few minutes and then cooled. This heating drives off water and adsorbed gases, and converts the small excess of Fe_2O_3 present almost completely into Fe_3O_4 . The residual gas was pumped out, and a known amount of pure oxygen was admitted. The charge was again heated at a definite rate. The magnetite began to oxidize at an observable rate at 300° . In some cases the temperature was held at 1100° until the pressure came to equilibrium; in others, the temperature was carried steadily up to 1200° .

The removal of oxygen in steps at 1200° was accomplished by closing the cut-off C, and pumping out the oxygen from the space between cut-off and stopcock. The quantity removed was known from the pressure and temperature of the gas in this space. The cut-off was then again opened and equilibrium reestablished by further dissociation of the iron oxide of the charge.

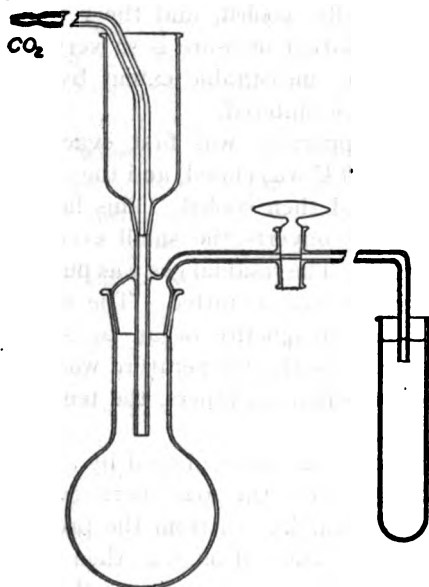
At the end of such a series the temperature was lowered at a definite rate, sometimes with a halt at 1100° for an additional measurement. The charge was removed at room temperature, weighed, and the ferrous oxide determined. The difference between the percentage of FeO so found and that calculated from the known amounts of oxygen removed was in nearly all cases less than 0.4%, and a correction for this difference was distributed among the calculated intermediate values for the composition of the oxide. The difference was probably brought about by small constant errors in the data for the volume or the temperature of the gas.

Methods of Analysis—Ferrous Oxide.—In the determination of ferrous oxide we have followed the method described by Blair¹ but with some details slightly modified. Blair's method consists essentially in the solution of the oxide in hydrochloric acid in an atmosphere of carbon dioxide, with subsequent titration with permanganate after the addition of zinc

¹ "The Chemical Analysis of Iron," 7th edition, p. 239.

sulfate. We would have preferred to use sulfuric acid as the solvent for the oxide, but the rate of solution of the oxides in this acid, even when crushed to pass 200 mesh, was so small as to exclude its use. This stability of otherwise readily soluble oxides is developed by the action of high temperatures.

Our apparatus in which the solution of the oxide is effected in an atmosphere of carbon dioxide is shown in Fig. 4. The flask has a capacity



of about 110 cc. The inlet tube for carbon dioxide is ground into the funnel tube and this joint serves as a valve for the introduction into the flask of liquid held in the funnel tube. The funnel tube is graduated at 10 and 25 cc. The advantages of an all-glass apparatus for this determination where all reducing substances must be rigorously excluded are evident.

While Blair uses zinc sulfate to eliminate the action of permanganate on the hydrochloric acid during titration we have preferred to use the ordinary "titrating mixture" of manganese sulfate, phosphoric acid and sulfuric acid.¹ For small amounts of ferrous oxide we used

Fig. 4.—Apparatus for determination of FeO. 0.01 *N* permanganate in volume burets while for larger amounts we weighed the 0.1 *N* permanganate used. All the solutions were standardized against Bureau of Standards sodium oxalate.

Total Iron.—Total iron was determined by reductions with zinc sulfur dioxide, and also with stannous chloride, the resulting ferrous iron being titrated with 0.1 *N* permanganate. When the reductions were made with zinc and with sulfur dioxide the sodium oxalate titer of the permanganate was employed; but this titer gave slightly high results with the stannous chloride reduction. Consequently, for the latter reduction, Bureau of Standards Ore No. 27 with total iron content of 69.2% was used as an empirical standard. The values for total iron reported in this paper are averages of a series of determinations by all three methods of reduction.

Using the convention, the results of analysis have been reported in the text as percentages of FeO on total weight of the oxide. This must

¹ *Bur. Standards Circ.* 26, 3d ed., p. 12.

not be understood as implying any opinion regarding the form of combination of ferrous iron in the solid phase. What is actually determined is of course the amount of iron which goes into solution in a form which will reduce permanganate. Whether or not FeO can actually exist free, whether or not FeO exists within the crystalline oxide, and whether or not there is any atomic distinction between ferrous and ferric iron inside of a crystal, are questions on which we have at present no information. For the present, therefore, the reporting of ferrous iron as FeO is to be considered simply as a convention.

Pressure-composition Isotherm at 1200° .—In Table III are recorded the results of numerous measurements of the oxygen pressure at 1200° , obtained (1) by heating Fe_2O_3 ; (2) by heating Fe_3O_4 with varying amounts of oxygen; (3) by withdrawing oxygen in known amounts from the oxide-oxygen system of (2); and (4) by withdrawing oxygen similarly from Fe_2O_3 with excess oxygen added.

The first column of the table contains the reference number of the series; the second gives the original weight of the charge in mg.; the third, the amount of oxygen added, in mg., calculated from the pressure, temperature, and volume of the furnace and gages.

The fourth column gives the equivalent volume of the apparatus at 1200° under the conditions of measurement. Since that portion of the gas which is within the furnace tube is heated to 1200° , its density is correspondingly diminished. In calculating the amount of gaseous oxygen this is allowed for by subtracting from the volume at room temperature the amount which the heated gas would contract if cooled to room temperature. This correction was calculated from the approximately known temperature distribution and was checked by measuring the actual increase of pressure produced in oxygen when the furnace was heated to various temperatures. Other smaller corrections to the volume were also made to allow for changes in level of the mercury columns caused by changes in barometer height and in the internal pressure.

The amount of oxygen present as gas was calculated from the volume corrected as above and the temperature of the apparatus. The latter was measured by means of six mercury thermometers hung at different points over the apparatus.

The fifth column contains the equilibrium pressure as measured, in mm. of mercury at 0° . The last column gives the percentage of the total iron which is in the "ferrous condition." This is calculated as follows: From the original weight and composition of the charge, the original amount of oxygen added, and the amount of oxygen remaining as gas in the apparatus, the amount actually combined in the charge can be calculated. A certain quantity of oxygen would have to be added to bring the charge up to the composition of Fe_2O_3 . The proportion of this

oxygen to the total in Fe_2O_3 , multiplied by 3, gives the "per cent. ferrous." For instance, the removal of 11.11% (one-ninth) of the total oxygen of Fe_2O_3 , yields magnetite, in which the "per cent. ferrous" is 33.33

TABLE III.
Oxygen Pressures at 1200°.

No.	Initial wt. charge. Mg.	Oxygen added. Mg.	Gas volume. cc.	Pressure. Mm.	Per cent. ferrous.	No.	Initial wt. charge. Mg.	Oxygen added. Mg.	Gas volume. cc.	Pressure. Mm.	Per cent. ferrous.
Magnetite.											
1562	1006.0	0	1265	0.041 ¹	33.43			35.37	1267	2.68	4.86
1545	1009.3	5.46	1462	1.00	30.60			32.25	1267	2.48	7.44
		5.13	2023	0.770	30.96	1536	999.4	29.29	1267	2.285	9.90
		4.12	2023	0.590	31.29			42.43	1464	3.98	1.93
		3.35	2023	0.460	31.56			41.15	1464	3.59	2.23
		2.75	2023	0.360	31.77			40.09	1464	3.37	2.75
1538	1003.3	13.26	1462	1.44	24.06			39.01	1464	3.13	3.23
		12.79	2063	1.27	25.29			38.00	1464	3.03	3.99
		11.13	1267	1.29	25.32	1532	1000.5	37.03	1464	2.87	4.81
		9.63	1266	1.17	26.49			44.95	1461	4.76	1.43
		8.27	1266	1.065	27.60			67.26	1463	13.09	0.61
		8.27	2023	0.965	28.59			63.05	1462	11.38	0.61
		7.01	2023	0.865	29.49			59.38	1462	9.92	0.63
		5.88	2023	0.759	30.18			56.18	1462	8.62	0.58
1516	1999.9	19.64	1454	1.355	25.41			53.40	1461	7.48	0.53
1551	1000.1	21.25	1461	1.855	17.27			50.99	1461	6.56	0.66
		20.65	1266	1.895	17.33			48.88	1461	5.78	0.85
		18.41	1266	1.75	19.19			47.02	1461	5.08	1.08
		18.41	2022	1.605	20.90			45.38	1461	4.50	1.32
		16.33	2022	1.46	22.43			43.93	1461	3.99	1.53
1554	1002.5	21.13	1462	1.79	17.31	1529	1002.4	42.65	1461	3.61	1.92
		20.55	1267	1.825	17.35	1521	1000.8	59.10	1455	10.23	0.97
		20.55	2023	1.68	19.18			80.46	1455	18.31	0.24
1548	1002.6	26.22	1460	1.86	12.60	Fe ₃ O ₄ from electrolytic iron.					
		25.62	2021	1.69	14.32	1595	1000.2	1271	2.54	5.64
		21.34	1265	1.595	16.04	1596	501.3	1271	2.055	9.00
		19.45	1265	1.49	17.58	1598	999.3	6.86	1396	3.64	1.94
		17.66	1265	1.395	19.06			6.09	1950	2.76	3.22
		17.66	2021	1.30	20.45			2.81	1950	2.38	5.20
1556	994.9	21.17	1462	1.56	16.56			—0.01	1950	2.18	7.34
		20.67	2023	1.45	18.11			—2.59	1950	2.08	9.58
		18.79	2023	1.37	19.64			—5.06	1950	1.99	11.74
		17.01	2023	1.275	20.98	Fe ₃ O ₄ Merck.					
1509	593.4	19.97	1451	2.43	10.50	1390	507.8	758	1.95	5.57
1512	996.6	20.09	1452	2.50	19.83	1391	497.0	758	1.385	3.88
1519	1001.5	40.03	1451	4.12	4.56	1392	497.5	758	1.65	4.63
1523	1126.5	39.60	1451	2.885	5.36	1394	499.6	758	1.61	4.53
1539	1000.5	41.85	1463	3.86	2.19	1398	489.2	758	1.95	5.37
		43.01	2024	3.21	2.73	Fe ₃ O ₄ Kahlbaum.					
						1503	504.0	758	2.07	5.46

¹ The larger part of this pressure is due to oxygen released by the reducing action of the platinum (see p. 813).

(one-third). The removal of 33.33% of the total oxygen of Fe_2O_3 would yield FeO , in which the "per cent. ferrous" is 100.

The data of Table III are shown graphically in Fig. 5. The form of the curve shows clearly that the dissociation pressure varies with the

Oxygen pressure in mm. mercury (logarithmic scale)

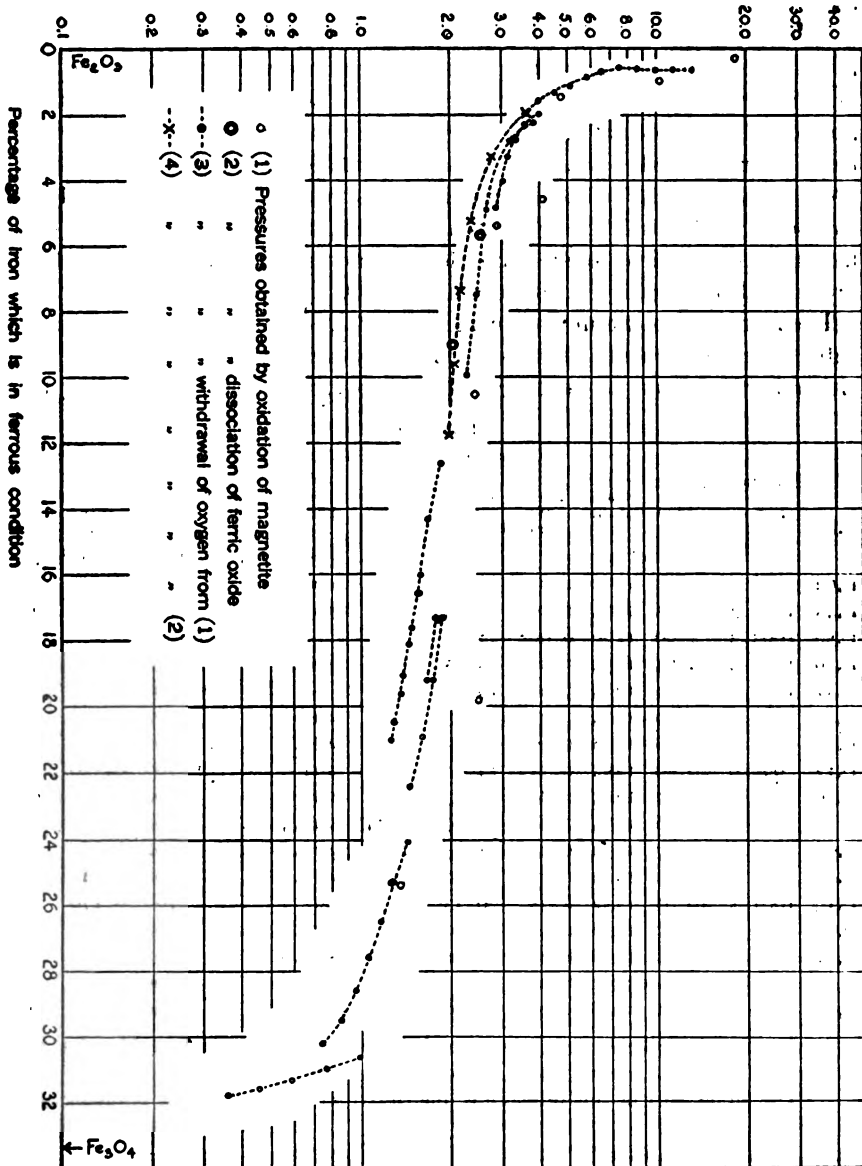


Fig. 5.—Pressure-composition isotherm at 1200°.

composition of the solid. Since this is a two-component system (iron and oxygen), there can be only one solid phase; in other words, there is a continuous solid solution series from Fe_2O_3 to Fe_3O_4 , or at least to a point very near Fe_3O_4 .

Fortunately this conclusion can be demonstrated optically for at least half the distance from Fe_2O_3 to Fe_3O_4 , as is shown later in more detail by Merwin's report.

This type of solid solution system, in which one of the two components is volatile while the two compounds which mix with one another differ only in the proportion of volatile component which is combined with the nonvolatile component, has few representatives among the systems that have been studied. One which is quite analogous is the series $\text{CoCl}_2 \cdot 6\text{NH}_3$ – $\text{CoCl}_2 \cdot 2\text{NH}_3$.¹ The ammonia pressures of this system fall continuously with diminishing content of NH_3 , following a reversed curve like that of the iron oxides, but less pronounced; near $\text{CoCl}_2 \cdot 2\text{NH}_3$ the pressure drops rapidly, as it does near Fe_3O_4 .

Pressure-composition Isotherm at 1100°.—Table IV contains the results of measurements at 1100°. These were, for the most part, made either in the course of heating a charge to 1200°, or during cooling from

TABLE IV.
Oxygen Pressures at 1100°.

No.	Initial wt. charge. Mg.	Oxygen added. Mg.	Gas volume. cc.	Pres- sure. mm.	Per cent. ferrous.	No.	Initial wt. charge. Mg.	Oxygen added. Mg.	Gas volume. cc.	Pres- sure. mm.	Per cent. ferrous.
Magnetite.						—5.06 1953 0.139 ³ 5.53					
1562	1006.0	0	1265	0.010 ³	33.36	1595	1000.2	1273	0.425	0.95
1545	1000.3	2.75	2023	0.100 ³	30.99	1596	501.3	1273	0.290	1.26
1558	1003.3	4.90	1266	0.068	28.71	Fe_2O_3 Kahlbaum.					
1516	1999.9	19.64	1455	0.075	23.85	1503	504.0	760	0.200	0.60
1551	1000.1	14.44	1265	0.094	19.49	Fe_2O_3 Merck.					
1548	1002.6	15.96	1264	0.084	18.73	1394	499.6	760	0.196	0.62
1554	1002.5	18.36	1268	0.102	15.79	1398	489.2	760	0.208	0.63
1512	996.6	20.09	1452	0.142	14.01	1369	204.9	760	0.120	0.85
1556	994.9	21.17	1465	0.084	12.93	1370	299.8	760	0.141	0.70
		15.36	1265	0.081	18.40	1374	295.4	760	0.120	0.60
1509	593.4	19.97	1452	0.248	1.65	1371	402.9	760	0.130	0.50
1523	1126.5	39.60	1449	0.710	0.66	1373	407.1	760	0.140	0.52
1519	1001.5	40.03	1452	2.35	0.23	1375	497.7	760	0.170	0.51
1529	1000.5	59.10	1458	10.04	0.30	1376	501.0	760	0.165	0.51
1521	1000.8	80.46	1456	18.24	0.12	1362	501.6	760	0.213	0.63
		Fe_3O_4 from electrolytic iron.				1365	1007.3	760	0.235	0.58
1598	999.3	6.86	1398	2.95	0.29	1367	1506.0	760	0.265	0.42

¹ Biltz and Fetkenbeuer, "Ammoniakverbindungen der Halogenide des zweiwertigen Kobalts," *Z. anorg. Chem.*, 89, 97–133 (1914).

² The larger part of this pressure is due to oxygen released by the reducing action of the platinum.

³ Pressure still falling.

1200°, the temperature being held at 1100° long enough for equilibrium to be established. The results are less reliable than those at 1200°, because the pressures are so much smaller that the effect of by-reactions becomes a much larger factor of uncertainty. Nevertheless, the pressures

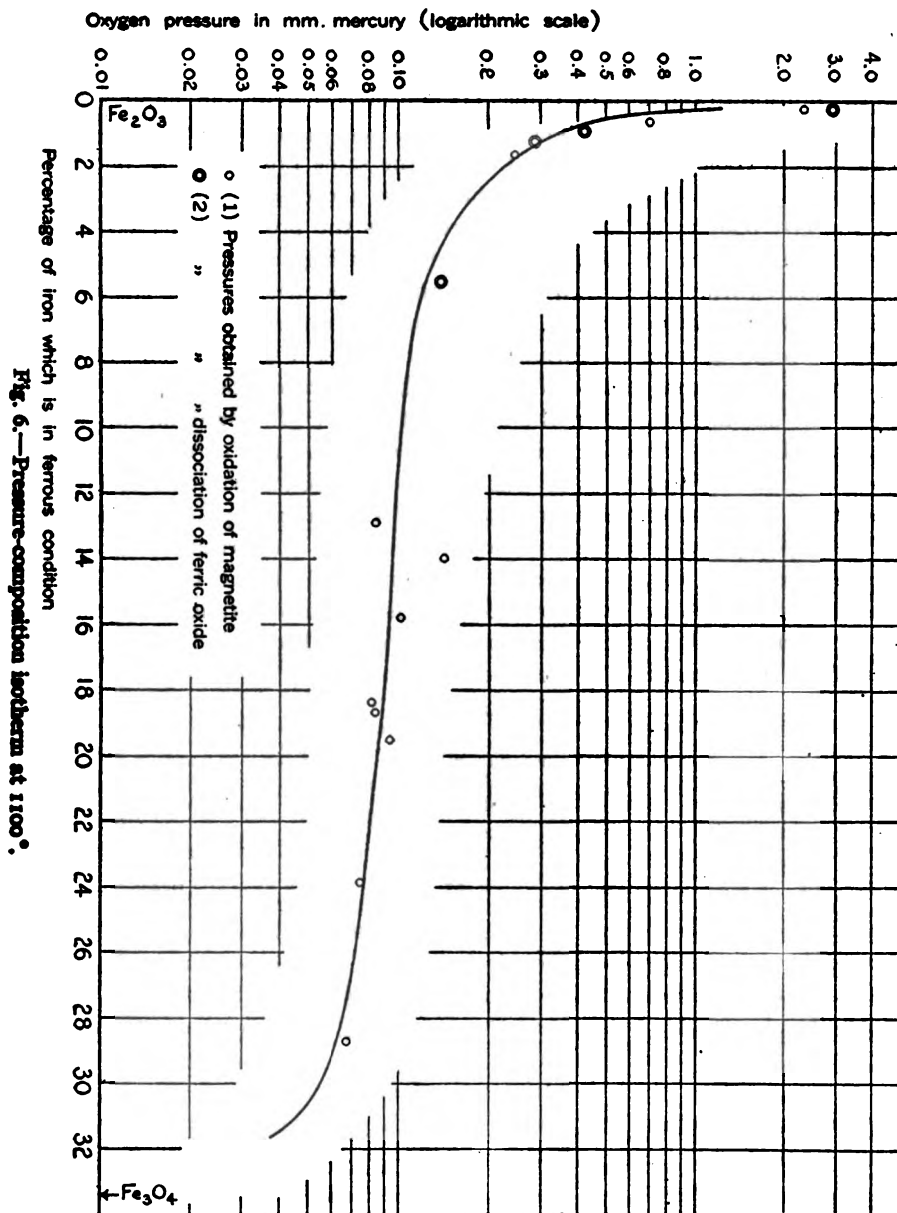


Fig. 6.—Pressure-composition isotherm at 1100°.

confirm in a general way the form of curve at 1200° , as may be seen from Fig. 6.

Form of Dissociation-pressure Curve near Fe_2O_3 .—The form of the dissociation-pressure curve near the ferric oxide side of the diagram is of interest. The evidence all points to a rapid rise of pressure near pure Fe_2O_3 ; in other words, the initial dissociation pressure of pure Fe_2O_3 is high, but drops rapidly as a small percentage of FeO appears in the oxide.

In addition to the data in Tables III and IV, the figures in Table V support this interpretation. These are data on approximately one-gram charges, all cooled from 1200° at about the same rate. The second column gives the amount of oxygen in the system in excess of the original Fe_2O_3 at the last reading at 1200° ; the third gives the pressure at 1200° ; the fourth, the amount of oxygen absorbed in cooling to room temperature, as calculated from the known volumes and temperatures of the gas space; and the fifth, the percentage of FeO found in the charge by analysis after its removal from the furnace. In every case a small amount of FeO is found in the charge after cooling. This indicates that there was at least this amount of FeO in the charge at 1200° . It might be supposed that the FeO was in the interior of some of the grains, to which oxygen had not had time to penetrate; but on lowering the temperature to 1100° , and then to room temperature, we found that a prompt absorption of oxygen took place, showing that some at least of the ferrous iron was in equilibrium with oxygen at 1200° , but immediately began to be oxidized when the temperature was lowered. It is significant that the amount of FeO left, as well as the amount of oxygen absorbed, is roughly inversely proportional to the pressure at 1200° .

TABLE V.

No.	Oxygen added.	Pressure at 1200° .	Oxygen absorbed	Percentage of FeO in product at 20° .
	Mg.		in cooling from 1200° to 20° . Mg.	
1521	80.46	18.31	0.27	0.14
1529	59.10	10.23	0.54	0.185
1532	42.65	3.61	1.76	0.24
1536	37.03	2.87	4.55	0.41

It is not surprising that on cooling to room temperature some of the ferrous iron did finally escape oxidation, for as the temperature is lowered the rates of diffusion and of oxidation rapidly diminish.

An observation by Baxter and Hoover during their work on the atomic weight of iron¹ is of interest in this connection. They ignited their oxide at a temperature which is estimated to be between 1000° and 1100° , both in air and in pure oxygen. The weight after ignition in oxygen was consistently 0.2 mg. (in 5 grams) higher than after ignition in air. This

¹ Baxter and Hoover, "A Revision of the Atomic Weight of Iron. V. The Analysis of Ferric Oxide," *THIS JOURNAL*, 34, 1657-1669 (1912).

was confirmed by repeated heating of the same charge, and again on another series of ignitions. Although the value for the atomic weight of iron, calculated from the oxygen ignition, is 55.840 as against 55.838 from FeBr_3 , whereas the air ignition yields the high value 55.847, nevertheless the authors ascribe the difference to "occlusion" of oxygen at the higher oxygen pressure. A more probable explanation, in view of our results, is that even under an oxygen pressure of 152 mm. (pressure of oxygen in air) there is a small amount of dissociation forming a very dilute solid solution of Fe_3O_4 in Fe_2O_3 ; this is driven back practically to zero by a full atmosphere of oxygen. The amount of FeO produced, if all the difference in weight observed is due to dissociation at the lower pressure, would be 0.036 per cent.; an amount which could hardly be detected analytically.

Optical Properties.¹—The synthetic Fe_2O_3 of Merck and of Kahlbaum consists in each case of aggregates of exceedingly small doubly refracting crystals. After being heated to 1200° in the vacuum furnace, under the oxygen pressure produced by its own dissociation, it is much more coarsely crystalline; the grains reach a maximum diameter of about 0.02 mm. Grains of magnetite of about this size may be oxidized to apparently homogeneous single grains of hematite.

The structure of similar grains which are not yet fully oxidized is shown in Fig. 7. Extinction is parallel to the structure. The dark or opaque skeleton consists presumably of a portion of the oxide which contains enough FeO to render it opaque in the thickness in which it is found in the grains. Such skeletons were found in Samples 1548, 1512, 1310 and 1536. In all these cases the amount of oxygen present was insufficient to oxidize the sample to Fe_2O_3 . Hence the rapid cooling from high temperatures was all the more likely to produce a certain amount of inhomogeneity, shown by the skeletons, as a result of the lack of opportunity for diffusion and reaction.

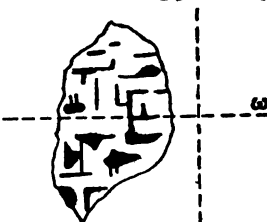


Fig. 7.—Skeletons of opaque oxide in transparent oxide, oxidized magnetite.

The observable optical properties² of the crystals of completely oxidized magnetite are not distinguishable from those of pure natural hematite, namely: uniaxial, negative, ϵ for $700\mu\mu = 2.74$, double refraction greater than 0.21, absorption of ω very slightly greater than that of ϵ . The products obtained by heating mixtures of Fe_2O_3 and Fe_3O_4 agree in optical characters with products having a similar content of FeO but made by other methods.

¹ Measurements by H. E. Merwin.

² Amorphous mixtures of selenium and tellurium were used as embedding materials for this series of preparations.

Preparations having compositions between pure Fe_2O_3 and a solution of the composition $\text{FeO } 22\% : \text{Fe}_2\text{O}_3 \text{ } 78\%$ appear optically as a single phase. A progressive darkening and a progressive lowering of the index n accompany increasing FeO . Beyond 18% FeO the absorption is so strong that optical study is not feasible. Oxide with 28% FeO (No. 1545), for instance, is completely opaque even in strong sunlight.

The results of the optical study are shown in Table VI.

TABLE VI.
Optical Properties.

No.	Material.	Treatment.	Final per cent. FeO .	n at $700 \mu\mu$.	$n - a$.
1503	Kahlbaum Fe_2O_3	Heated at 1200°	0.58	2.74	>0.21
1314	{ 5% Fe_2O_4 95% Merck Fe_2O_3	Heated at 1200°	5.60	2.73
1512	$\text{Fe}_2\text{O}_4 + \text{O}_2$	Heated at 1200°	12.99	2.72
1548	$\text{Fe}_2\text{O}_4 + \text{O}_2$	Heated at 1200°	16.11	2.71	>0.16
1310	{ 50% Fe_2O_4 50% Merck Fe_2O_3	Heated at 1200°	17.79	2.71

The refractive index of magnetite has been determined by a reflection method by Loria and Zakrzewski,¹ who found n to be 2.42 for a wave length of $700 \mu\mu$. The refractive indices of hematite should therefore be lowered by dissolved Fe_2O_4 , as is found to be the case. The observed lowering, however, is far from being proportional to the amount of Fe_2O_4 in solution. The optical properties, therefore, confirm the existence of solid solution between hematite and magnetite over the range, within which the products are reasonably transparent (0–18% FeO), and unless the curve of index against composition changes direction rapidly, would indicate a separation into two phases at some point between 18% FeO and pure Fe_2O_4 . The pressure-composition isotherm indicates that solid solution continues at least as far as 31.8% ferrous. If there is a break, then, it must be expected between 31.8 and 33.33% ferrous, that is, within 1.5% of pure magnetite.

Comparison with Previous Investigations.

Since the dissociation pressure depends upon the composition of the solid phase, it is easy to see why there has been so much uncertainty about the value of the dissociation pressure of Fe_2O_3 . The pressure obtained depends not only upon the temperature, but also upon the relation of weight of charge to volume of gas space. The data of Walden,² for instance, which are frequently quoted, have very little quantitative significance because the weight of charge and volume of gas are not stated, and the oxide whose pressure is being measured is different for each temperature. Hilpert³ suspected some years ago, after many unsatisfac-

¹ Loria and Zakrzewski, *Ans. Akad. Wiss. Krakau*, 1910, 278–286.

² P. T. Walden, *THIS JOURNAL*, 30, 1350–1355 (1908).

³ S. Hilpert, *Ber.*, 42, 4893–4895 (1909).

tory experiments by the kinetic (gas-current) method, that the difficulty lay in the formation of intermediate compounds between Fe_2O_3 and Fe_3O_4 . He found that the dissociation pressure varied with the source and condition of the Fe_2O_3 employed. This is to be expected when the pressure is determined kinetically in a solid solution system, for the result will depend to a large extent upon the fineness of the powder and the condition of the surface of the grains.

Kohlmeyer¹ has made cooling curves on Fe_2O_3 heated rapidly to its "melting point" and interprets the results as indicating the existence of compounds $\text{FeO} \cdot 3\text{Fe}_2\text{O}_3$, $3\text{FeO} \cdot 5\text{Fe}_2\text{O}_3$, and $3\text{FeO} \cdot 4\text{Fe}_2\text{O}_3$, as well as inversion points² in Fe_2O_3 at 1028 – 1035° and 1250 – 1350° . We have found no direct thermal or other evidence either of compounds or inversion points above 1000° .

Differential heating curves on Kahlbaum's and Merck's pure Fe_2O_3 do, however, show a sharp inversion point at 678° , and a barely detectable irregularity between 755° and 785° . The latter may be due to an inversion point corresponding to the A₂ point in pure iron. The A₂ point has been shown by electrical resistance measurements on pure iron³ to occur at 757° , and by thermal curves on the same iron,⁴ at 768° . These points are in the temperature region in which iron becomes practically non-magnetic. If there is in fact an inversion in Fe_2O_3 , which corresponds with that in pure iron, the inversion would seem to have some atomic basis, and would not, as suggested by Burgess and Crowe,⁵ depend entirely upon a crystallographic change of the type of A₃ (at 898 – 909°).

The only remaining oxide indicated between Fe_2O_3 and Fe_3O_4 is the Haber-Kaufmann oxide⁶ $2\text{FeO} \cdot 3\text{Fe}_2\text{O}_3$. This is said to be a well-defined compound when prepared at ordinary temperatures and can be dried at 180° , but according to Chandra⁷ it is unstable at higher temperatures. We find no indication of its existence at 1100° and 1200° .

Further investigations are under way on the magnetic properties of the Fe_2O_3 – Fe_3O_4 series, the inversions in Fe_2O_3 and Fe_3O_4 , and the melting points and oxygen pressures in the system Fe_3O_4 –Fe. The geological and mineralogical application of these data will be presented in a later paper.⁸

¹ E. J. Kohlmeyer, *Met. u. Erz.*, **1**, 447–462 (1913).

² E. J. Kohlmeyer, *Metallurgie*, **6**, 323–325 (1909).

³ Burgess and Kellberg, *Bull. Bur. Standards*, **11**, 457–470 (1914).

⁴ Burgess and Crowe, *Ibid.*, **10**, 315–370 (1913).

⁵ *Op. cit.*, 1913, p. 367.

⁶ Kaufmann, *Z. Elektrochem.*, **7**, 733–741 (1901).

⁷ H. Chandra, *Inaug. Diss.*, Berlin, 1913.

⁸ A preliminary report on the ferrous iron content and magnetic properties of the natural oxides of iron was presented at the December, 1915, meeting of the Geological Society of America.

Summary.

This investigation of the chemical relationships of the iron oxides has been undertaken as a basis for the study of the iron-bearing silicates at high temperatures. Measurements of the dissociation pressure of the iron oxides were made in a vacuum furnace with a heating tube of platinum-rhodium.

A study of the conditions of equilibrium shows that reproducible oxygen pressures can be obtained at a given temperature. Equilibrium is attained in a few minutes at high temperatures, although certain disturbing reactions go on slowly. One of these by-reactions is the reduction of the oxide by platinum, yielding oxygen and an iron-platinum alloy. This reaction accounts for the common occurrence of iron as an impurity in platinum.

Ferric oxides from various sources yield practically identical pressures (excluding certain minor exceptions which cannot as yet be explained). The same pressures are also attained on both rising and falling temperatures. The oxidation of magnetite gives pressures which are identical with those produced by dissociation of pure Fe_2O_3 .

The pressure-composition isotherm for the system Fe_3O_4 - Fe_2O_3 at 1200° indicates a continuous solid solution series from Fe_3O_4 over to a point very near Fe_2O_3 , if not over the entire range to Fe_2O_3 . The opacity of the products prevents an optical demonstration of the existence of solid solution in products with more than 18% FeO , but its existence can be shown optically in products which are more ferric than this. The pressure-composition isotherm at 1100° confirms that at 1200° .

The major portion of the oxygen pressure curve of the system at 1200° lies between the limits 4 mm. and 1 mm. The pressure drops rapidly near Fe_3O_4 , and raises rapidly near Fe_2O_3 . Table VII contains a series of representative values.

TABLE VII.

Representative values of oxygen pressure in equilibrium with solid solutions between Fe_2O_3 and Fe_3O_4 .

Percentage of FeO .	Percentage of iron which is ferrous.	Pressure at 1100° .	Pressure at 1200° .
0.90	1.0	0.37	5.0
1.80	2.0	0.22	3.6
2.71	3.0	0.17	3.0
4.52	5.0	0.13	2.6
9.09	10.0	0.10	2.15
13.70	15.0	0.092	1.80
18.37	20.0	0.085	1.55
23.07	25.0	0.069	1.27
27.83	30.0	0.052	0.85
31.03	33.33	<0.005	<0.04

Since the dissociation of Fe_2O_3 results in the formation of a solid solution, the pressure of oxygen and the composition of the solid phase depend upon the relation of the weight of the charge to the volume of the space into which the oxygen dissociates. This fact accounts for the variety and uncertainty of results heretofore obtained in experiments on the dissociation pressure of Fe_2O_3 .

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY.]

THE VISCOSITY OF CERTAIN ALCOHOLIC SOLUTIONS.

By O. F. Tower.

Received February 22, 1916.

About a year ago the author, in collaboration with Dr. Germann,¹ published the results of a series of determinations of the vapor pressures of solutions of three typical solutes in methyl and ethyl alcohols. It has seemed worth while to investigate in addition some of the other physical properties of such solutions. The electrical conductivity of those that are conductors have already been measured, so in this paper the results of viscosity determinations are given, together with a general discussion of the relations existing between the viscosity and other physical properties of such solutions.

The solutes were the same as those employed in the vapor-pressure determinations, *viz.*, lithium chloride, potassium iodide and benzil; and in addition urea, since vapor pressures of solutions of this substance in ethyl alcohol have recently been published.² The urea used was a pure preparation and was further purified by two crystallizations from hot absolute alcohol; the other solutes were from samples which had been purified for the vapor tension work. They were all preserved after purification in a vacuum desiccator. The alcohols were purified by allowing "C. P." preparations to stand in contact with quick-lime for a year, after which they were distilled on to anhydrous copper sulfate and remained in contact with it for somewhat over a week. After this they were fractionated *in vacuo* in an apparatus like that described in the previous paper, and were then distilled, still *in vacuo*, on to weighed quantities of the solute. The solutions thus obtained were transferred to the viscosimeter by means of an apparatus essentially the same as that employed by Thorpe and Roger³ for the same purpose, and were therefore in contact with ordinary air only for the moment they were being transferred from the distilling apparatus. In the viscosimeter they were in contact only with air which had been dried over phosphorus pentoxide.

¹ THIS JOURNAL, 36, 2449 (1914).

² Price, *J. Chem. Soc.*, 107, 188 (1915).

³ *Phil. Trans.*, (A) 185, 415 (1894).

The viscosimeter used was a modified form of the Bingham apparatus (see Fig. 1). It had two vertical capillary tubes about 5 cm. long, one in each arm of the instrument, instead of one horizontal, removable capillary as in the apparatus employed by Bingham and White.¹ Its total capacity

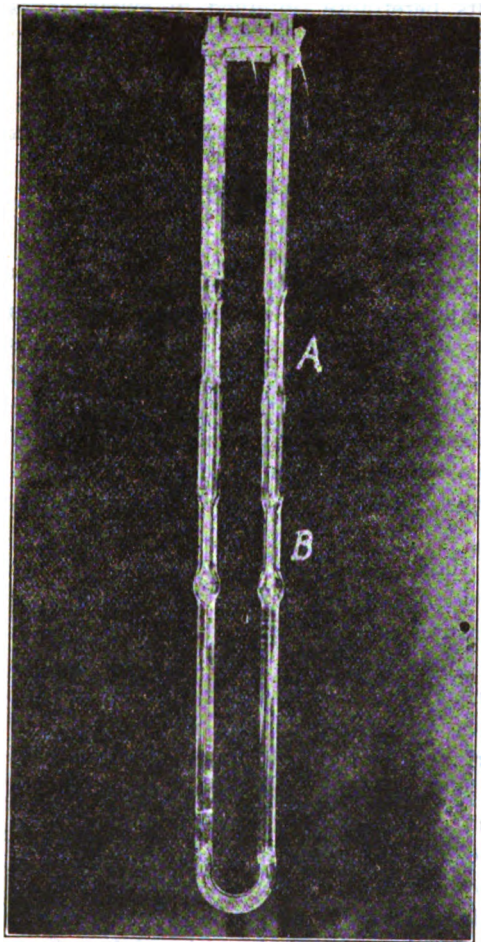


Fig. 1.

while in operation was 5 cc. It stood in a water bath with glass sides of about 10 liters capacity, whose temperature could easily be maintained within 0.1° of the desired temperature, usually 15° . Each arm of the viscosimeter was connected with an outlet of a four-way stopcock. The other outlets of the stopcock connected with the external air and with an air chamber, respectively. The air in the chamber was maintained at constant pressure by means of a column of water equivalent to 47 mm. of mercury. A large tube containing phosphorus pentoxide separated the air in contact with the water column from the main air chamber. In carrying out an experiment the liquid in the instrument was driven from A to B (see Fig. 1) or *vice versa* by means of the constant air pressure, the time being measured with a stop-watch.

The apparatus was calibrated by using specially purified water, whose viscosity at 15° was assumed to be 0.01136, which is the average of the

results of Thorpe and Roger² and of Bingham and White.³ To illustrate the slight variations observed in the time of flow, one set of the results with water are given in Table I.

¹ *Z. physik. Chem.*, **80**, 684 (1912).

² *Loc. cit.*

³ *Ibid.*, Hosking's value at this temperature is 0.01142, *Phil. Mag.*, [6] **18**, 260 (1909). This seems to be too high.

TABLE I.

Emptying.		Filling.	
Min.	Sec.	Min.	Sec.
5	33	5	28
5	32.5	5	29
5	33	5	29
5	32	5	28.5
5	33.5	5	28
5	33	5	28.5
Average.....5		5	28.5
Average both sides, 5 min., 30.7 sec. = 330.7 sec.			

Since the driving force due to the weight of the liquid was negligible in comparison with the pressure exerted by the water column,¹ we have for any two liquids, $\eta/\eta' = t/t'$, in which η and η' are the viscosities and t and t' are the times of flow of the two liquids, respectively. For water at 15°, $\eta' = 0.01138$, and $t' = 330.7$ sec. (see Table I); therefore for any other liquid $\eta = \eta'/t' t = 0.00003435 t$, which is the equation used in calculating the viscosities in all of the following work.

The viscosity of methyl and ethyl alcohols has been previously determined, as well as that of mixtures of these alcohols with water for every 5 or 10% change of concentration up to pure water.² These results have been plotted in curves showing the variation in the viscosity with increasing quantities of water. However, no determinations have been made between the viscosity of pure alcohol and that of a mixture containing about 5 or 10% of water. This is a portion of the curve which it is very desirable to know as accurately as possible, and hence I have determined not only the viscosity of the alcohols themselves, but also that of mix-

TABLE II.

Methyl alcohol.		Ethyl alcohol.		Temperature.	Methyl alcohol.		Observer.
% water by wt.	Viscosity. η .	% water by wt.	Viscosity. η .		% water by wt.	η .	
0.0	0.006292	0.0	0.01317	14.53°	0.0	0.006405	T. & R. ³
0.762	0.00652	0.775	0.01383	15°	0.0	0.00638	Getman (⁴)
1.230	0.00671	1.876	0.01443	15°	12.24	0.00965	"
2.477	0.00708	4.115	0.01545	...	Ethyl alcohol.		
4.653	0.00782	6.764	0.01678	13.23°	0.0	0.013573	T. & R. ³
8.103	0.00891	9.267	0.01805	15°	0.0	0.01315	B. & D. ⁵
11.210	0.00995	11.104	0.01891	15°	6.22	0.0166	V. & G. ⁶
15.142	0.01111	12.974	0.01973	15°	12.275	0.0189	"

¹ Several experiments showed this to be true.

² See for example Dunstan, *J. Chem. Soc.*, 85, 823-4 (1904); and Getman, *J. chim. phys.*, 4, 386 (1906).

³ Thorpe and Rodger, *loc. cit.*, pp. 530-1.

⁴ *Loc. cit.*, pp. 392 and 395. Given in the text as 10% water by volume.

⁵ Bingham and White, *loc. cit.*, p. 282.

⁶ Varenne and Godefroy, *Compt. rend.*, 137, 9931 (1903). Results have been recalculated to the same units as the others in this paper.

tures of them with small quantities of water. The measurements were made at 15° , and the results are given in Table II. Results obtained by others at or near the same temperature are shown at the right. Those with methyl alcohol differ considerably from mine. This is probably due to the fact, that so-called C. P. methyl alcohol is not as pure as absolute ethyl alcohol, not because it contains more water, but because it very likely contains traces of other organic substances, from which it is freed only by repeated fractional distillation. This was insured in the sample used here by the rigorous fractioning to which the alcohols were subjected *in vacuo*.

The results of Table II have been plotted in curves, which are reproduced in Fig. 2. The viscosities of the ethyl alcohol mixtures have been

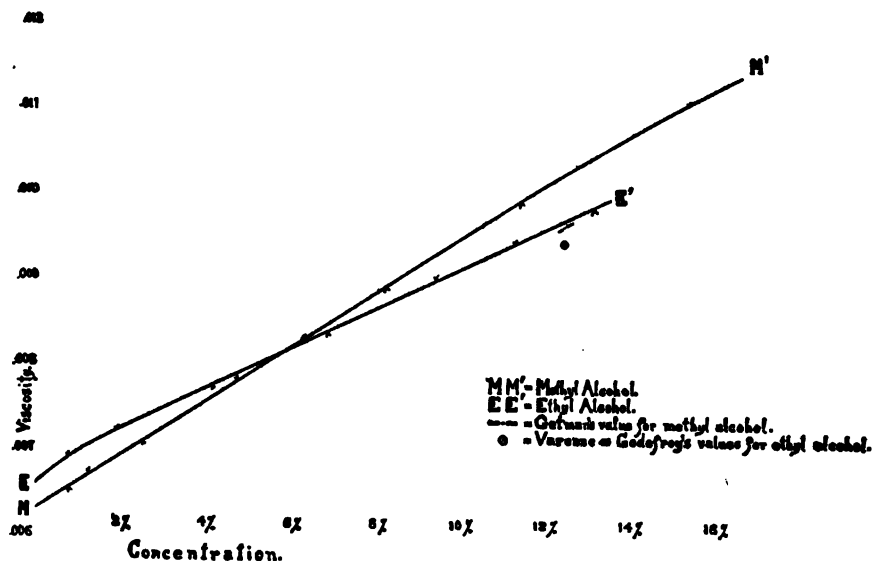


FIG. 2.

divided by two, and the numbers so obtained used as ordinates. This was done so that both curves could be shown on the same diagram. As is seen, they both approximate to straight lines, so that there is nothing exceptional in the "alcohol end" of the viscosity curves of mixtures of water with either methyl or ethyl alcohol.

The results of the viscosity measurements, which have been made at 15° (the temperature at which the vapor pressure determinations were made), are shown in Table III. The reciprocal of the viscosity is known as the fluidity. This is shown under ϕ in the last column.

Table IV gives the results using urea as solute. The measurements were made at different temperatures as indicated by the subscripts in the viscosity and fluidity columns.

TABLE III.—OBSERVATIONS AT 15°.

Solvent: Methyl Alcohol.				Solvent: Ethyl Alcohol.			
Solute: Lithium Chloride.				Solute: Lithium Chloride.			
Substance in 1 g. alcohol.	Mol. per mol.	η .	ϕ .	Substance in 1 g. alcohol.	Mol. per mol.	η .	ϕ .
0.06843	0.05170	0.01471	67.98	0.04516	0.04904	0.02998	33.36
0.04479	0.03386	0.01118	89.45	0.03501	0.03802	0.02486	40.23
0.02756	0.02082	0.009114	109.7	0.02093	0.02273	0.01977	50.58
0.01459	0.01102	0.007815	128.0	0.01048	0.01138	0.01643	60.86
0.01392	0.01052	0.007729	129.4	0.004824	0.005236	0.01477	67.70
0.00792	0.005983	0.007207	138.8	0.002587	0.002809	0.01405	71.17
0.00490	0.003703	0.006891	145.1				
0.002655	0.002005	0.006667	150.0				
Solute: Potassium Iodide.				Solute: Potassium Iodide.			
0.11694	0.02238	0.00823	121.5	0.01337	0.003709	0.01386	72.15
0.07674	0.01481	0.00768	130.2	0.00880	0.002274	0.01362	73.42
0.04574	0.00883	0.00717	139.5	0.00474	0.001315	0.01342	74.52
0.02265	0.00437	0.00674	148.4				
0.01187	0.00229	0.006565	152.3				
0.00574	0.00111	0.006465	154.7				
Solute: Benzil.				Solute: Benzil.			
0.04293	0.006545	0.006661	150.1	0.02039	0.004470	0.01335	74.91
0.03112	0.004745	0.006589	151.8	0.01136	0.002490	0.01328	75.30
0.01889	0.002880	0.006479	154.3	0.00682	0.001495	0.01322	75.64
0.01094	0.001668	0.006410	156.0				

TABLE IV.—UREA AS SOLUTE.

Solvent: Methyl Alcohol.						
Substance in 1 g. alcohol.	Mol. per mol.	η_{25}° .	η_{35}° .	η_{40}° .	η_{50}° .	
0.09154	0.04882	0.006690	149.5	0.005493	182.1	
0.06110	0.03258	0.006435	155.4	0.005155	194.0	
0.04335	0.02312	0.006183	161.7	0.004964	201.5	
0.02986	0.01592	0.005968	167.6	0.004819	207.5	
0.01567	0.008355	0.005771	173.3	0.004663	214.5	
0.008693	0.004636	0.005665	176.5	0.004558	219.4	
Pure alcohol.....		0.005523	181.1	0.004460	224.2	
Solvent: Ethyl Alcohol.						
Substance in 1 g. alcohol.	Mol. per mol.	η_{25}° .	η_{35}° .	η_{40}° .	η_{50}° .	Mol. per mol.
0.04749	0.03641	0.01243	80.5	0.007762	128.8	0.04875
0.03163	0.02435	0.01195	83.7	0.007535	132.7	0.03804
0.01432	0.01098	0.01140	87.7	0.007301	137.0	0.03005
0.007395	0.00567	0.01121	89.2	0.007164	139.6	0.01836
						0.01095
						0.006659
						0.003712
Pure alcohol.....		0.01098	91.1	0.007040	142.1	0.008382
						119.3

In order to ascertain how the viscosity of these solutions varies with change of temperature, the following measurements were made at the temperatures indicated by the subscripts (Table V):

TABLE V.
Potassium Iodide in Methyl Alcohol.

Substance in 1 g. alcohol.	Mol. per mol.	η_{25}° .	η_{35}° .	η_{40}° .	η_{45}° .
0.09772	0.01885	0.006767	147.8	0.005443	183.7
0.07039	0.01358	0.006450	155.0	0.005207	192.0
0.03593	0.006933	0.006018	166.2	0.004864	205.6
0.01786	0.003445	0.005782	173.0	0.004661	214.6

Benzil in Methyl Alcohol.

Substance in 1 g. alcohol.	Mol. per mol.	η_{40}° .	η_{45}° .
0.05477	0.00835	0.004880	204.9
0.03337	0.00509	0.004727	211.5
0.02010	0.003065	0.004624	216.3
0.01074	0.001637	0.004552	219.7

Benzil in Ethyl Alcohol.

Substance in 1 g. alcohol.	Mol. per mol.	η_{40}° .	η_{45}° .
0.04717	0.01934	0.008723	114.6
0.03824	0.008383	0.008659	115.5
0.02574	0.005642	0.008566	116.7
0.01206	0.002644	0.008472	118.0

The variation of the viscosity with the concentration of those solutions of which the measurements were made at 15° and of the urea solutions at 40° is shown in the form of curves in Fig. 3.

These curves show that each solute affects the viscosity of both alcohols in a very similar manner. The steepness of the curve depends obviously on the solvation of the solute. Lithium chloride combines to a considerable extent with the alcohols and its curves are therefore the most inclined, potassium iodide which combines to a less extent gives curves of intermediate slope, while the curves of benzil and urea which do not combine with the solvent to any extent are quite flat. Of course also, in the case of the first two solutes besides combination with the solvent, ionization takes place, which renders interpretation of the results more difficult.

According to Bousfield¹ the viscosity of a solution is proportional to the radions of the different substances composing the solution. By radion he denotes the average molecular radius of a given species of molecules, as, for example, those of water, in the forms of hydrol, dihydrol and trihydrol. His expression for the viscosity is then, $\eta = C_1 B_1 r_1 + C_2 B_2 r_2 + \text{etc.}$ in which $C_1, C_2, \text{etc.}$, are constants and $B_1, B_2, \text{etc.}$, are the volume fractions occupied by a set of molecules whose radions are $r_1, r_2, \text{etc.}$, respectively. Now in aqueous solution, on account of the association of the solvent, the value of r may undergo great changes due to the action of the solute on the three kinds of water molecules. The alcohols are less associated than water, and consequently one might expect a solute to have less effect in altering the average molecular size, that is, in altering their radions. This being the case, the change in

¹ *Phil. Trans.*, (A) 206, 134 (1906), and also *J. Chem. Soc.*, 107, 1781 (1915).

viscosity of a given solution with the concentration should depend more upon the solute and its changes in solvation and ionization than upon the solvent; and this is what the curves of Fig. 3 seem to show. In aqueous solution these solutes have a very different effect upon the viscosity.

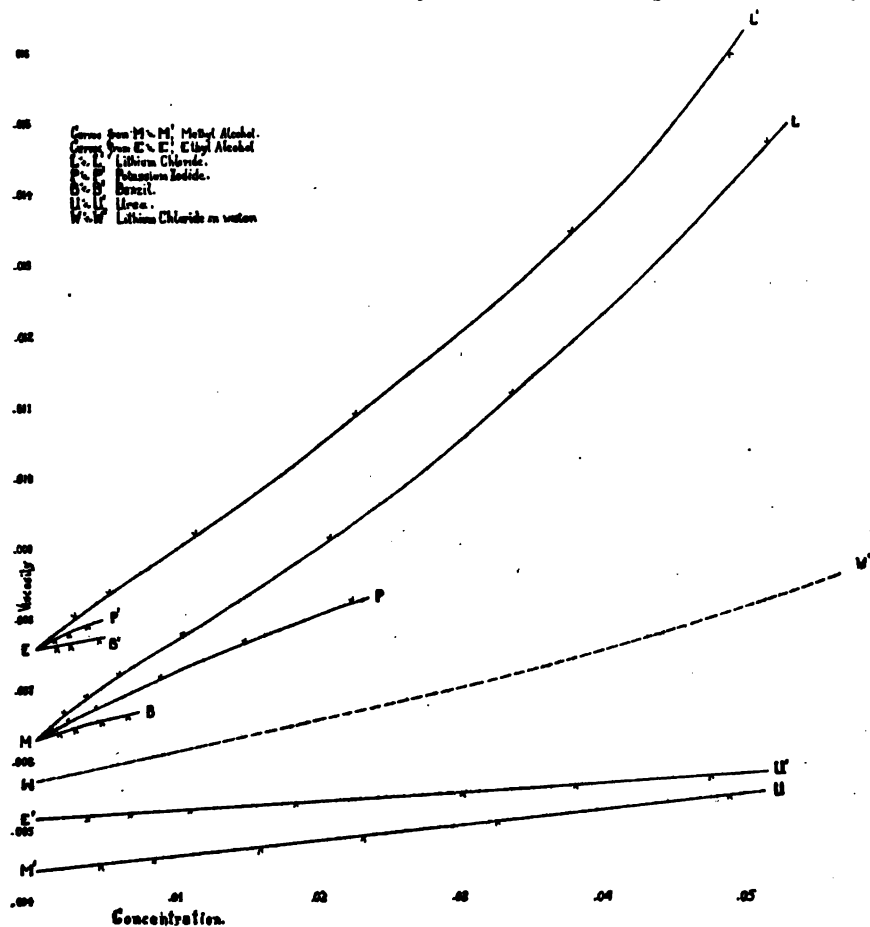


Fig. 3.—The scale of viscosities is that of the solutions in methyl alcohol. In order to show the results in ethyl alcohol solution on the same diagram, the viscosities of such solutions have been halved and then 0.001 added. This last was done so that the curves would not be superimposed upon those of the methyl alcohol solutions. For example, the viscosity of pure ethyl alcohol at 15° is 0.01317; one-half of this is 0.00659, and adding 0.001 we obtain 0.00759, which is the point E in the left-hand margin. All ordinates for the ethyl alcohol solutions were obtained in the same manner.

As is well known, potassium iodide and a number of other salts of caesium, rubidium, potassium and ammonium, when dissolved in water, yield solutions with negative viscosities, and also the viscosity curve of lithium

chloride in water¹ (shown as a dotted line in Fig. 3) is very unlike the ones here obtained when it is dissolved in alcohols.

The viscosity of a solution is a resultant of a number of forces, of which one of the principal is the same as that which determines the vapor tension. Vapor tension is due to the motion of the molecules of a liquid and the consequent escape of some of them from the surface of the liquid into the vapor state; and in general the more viscous a liquid the less is its vapor tension. The expression, $p - p_1/\rho c$, that is, the relative lowering of the vapor pressure divided by the concentration is a characteristic constant for solutions. It is known that the similar expression for the viscosity, viz., $\eta' - \eta/\eta c^2$ is not characteristic of aqueous solutions. However, for the reasons advanced above, in the case of alcoholic solutions such an expression might be constant and might show some relation to the vapor-pressure lowering constant. To test this these two expressions have been evaluated for the alcoholic solutions considered in this paper in so far as vapor-pressure measurements are available. The results are shown in Table VI.

The fluidity of a solution has sometimes been found to be more intimately related to certain other of its physical properties than has the viscosity. Consequently for the solutions of lithium chloride in the alcohols the numerical values of the expression $\phi - \phi'/\rho c$ are given also. It is seen, however, that these values are not so constant as those under the similar expression for the viscosity, and hence space will not be consumed in giving these values for the remainder of the solutions. The vapor pressures of the lithium chloride, potassium iodide and benzil solutions are taken from the work of Tower and Germann,² and of the urea solutions from the work of Price.⁴ In the former case the viscosities have been read off from the curves of Fig. 3, at the concentrations at which the vapor pressures were measured, and in the latter case the reverse method has been employed, that is, the vapor pressures have been taken from Price's curves at the concentrations at which the viscosities were determined. The values of the viscosity are not repeated in the following table unless they are interpolated values not previously given. The viscosity, η , of the pure alcohols will be found in the previous tables. The following are the values used for p , the vapor pressure of the pure solvents:

Methyl alcohol, 15°, 73.61 mm.

Ethyl alcohol, 40°, 134.95 mm.

Ethyl alcohol, 15°, 32.18 mm.

Ethyl alcohol, 50°, 224.8 mm.

The concentration c is expressed in mols per mol, and the temperature is 15° unless indicated otherwise by a subscript.

¹ Data from Hoaking, *Phil. Mag.*, [6] 7, 472 (1904).

² In this expression η' is the viscosity of the solution and η that of the pure alcohol.

³ *Loc. cit.*, pp. 2454-5.

⁴ *Ibid.*, pp. 191-3.

TABLE VI.

Solute: Lithium Chloride.

Solvent: Methyl Alcohol.

Solvent: Ethyl Alcohol.

c.	ρ'	η'	$\frac{\rho-\rho'}{\rho c}$	$\frac{\eta'-\eta}{\eta c}$	$\frac{\rho-\rho'}{\rho c}$	c.	ρ'	η'	$\frac{\rho-\rho'}{\rho c}$	$\frac{\eta'-\eta}{\eta c}$	$\frac{\rho-\rho'}{\rho c}$
0.04103	67.85	0.01250	1.91	24.1	12.1	0.04156	30.385	0.02632	1.34	24.0	12.0
0.03150	69.27	0.01082	1.87	22.9	13.3	0.02268	31.0215	0.01974	1.59	22.0	14.7
0.02032	70.950	0.00905	1.78	22.1	15.0	0.01875	31.4262	0.01854	1.26	21.8	15.5
0.01298	71.870	0.00807	1.82	21.8	17.0	0.01289	31.6930	0.01687	1.18	21.8	17.0
0.00724	72.6035	0.00733	1.88	22.8	19.6	0.01024	31.8403	0.01618	1.03	22.3	18.2
0.00468	73.0229	0.00700	1.70	24.1	21.5						
0.00185	73.4652	0.00665	1.06	30.9	28.9						

Solute: Potassium Iodide.

Solvent: Methyl Alcohol.

c.	ρ'	η'	$\frac{\rho-\rho'}{\rho c}$	$\frac{\eta'-\eta}{\eta c}$	c.	ρ'	η'	$\frac{\rho-\rho'}{\rho c}$	$\frac{\eta'-\eta}{\eta c}$
0.02444	70.692	0.00837	1.62	13.5
0.01489	71.830	0.00769	1.62	14.9
0.00942	72.487	0.00721	1.62	15.5	0.01885	11.95	11.70		
0.00630	72.812	0.00693	1.72	16.2	0.01358	12.36	12.83		
0.00333	73.187	0.00665	1.73	17.2	0.006933	12.93	12.48		
0.00119	73.456	0.00647	1.76	24.0	0.003445	13.61	13.08		

Solute: Potassium Iodide.

Solvent: Ethyl Alcohol.

c.	ρ'	η'	$\frac{\rho-\rho'}{\rho c}$	$\frac{\eta'-\eta}{\eta c}$	c.	ρ'	η'	$\frac{\rho-\rho'}{\rho c}$	$\frac{\eta'-\eta}{\eta c}$
0.00463	31.9903	0.01399	1.27	13.5
0.00273	32.0673	0.01372	1.27	15.2
0.00170	32.1172	0.01355	1.15	17.0

Solute: Benzil.

Solvent: Methyl Alcohol.

0.00558	73.278	0.00662	0.81	9.4	0.00835	11.3
0.00479	73.290	0.006595	0.91	10.1	0.00509	11.8
0.00315	73.418	0.006505	0.83	10.8	0.003065	12.0
0.00161	73.510	0.00640	0.84	10.9	0.001637	12.6

Solute: Benzil.

Solvent: Ethyl Alcohol.

0.00619	31.992	0.01339	0.99	2.70	0.01034	3.94
0.00338	32.061	0.01332	1.09	3.37	0.008383	3.94
0.00175	32.121	0.01325	1.05	3.47	0.005642	3.89
...	0.002644	4.06

Solute: Urea.

Solvent: Methyl Alcohol.

Solvent: Ethyl Alcohol.

c.	$\frac{\eta'-\eta}{\eta c_{25}}$	$\frac{\eta'-\eta}{\eta c_{40}}$	c.	ρ'_{40}	$\frac{\rho-\rho'}{\rho c_{40}}$	$\frac{\eta'-\eta}{\eta c_{40}}$	c.	η'_{25}	ρ'_{40}	$\frac{\rho-\rho'}{\rho c_{40}}$	$\frac{\eta'-\eta}{\eta c_{40}}$
0.04882	4.33	4.74	0.04875	126.8	1.24	2.97
0.03258	5.07	4.78	0.03804	128.6	1.24	2.95	0.03641	3.63	214.5	1.26	2.81
0.02312	5.17	4.89	0.03005	130.3	1.23	2.95	0.02425	3.64	217.74	1.27	2.90
0.01592	5.06	5.06	0.01836	132.2	1.10	2.99	0.01098	3.48	221.81	1.21	3.38
0.008355	5.38	5.45	0.01095	133.5	0.98	2.89	0.00567	3.69	222.84	1.50	3.11
0.004636	5.55	4.74	0.00666	2.87

Considering first the observations at 15° , it is seen that the value of the expression $\eta' - \eta/\eta c$ is a constant for any one substance within the limits of error of the measurements. To avoid frequent circumlocution this will be termed the "viscosity constant," and for the same reason the expression $p - p'/pc$ will be known as the "vapor-pressure constant." The former does not vary much with the nature of the alcohol except in the case of benzil, where it has a much greater value in methyl alcohol than in ethyl. In connection with the calculations of the molecular weights from the lowering of the vapor pressure it was remarked: "The molecular weight of benzil in ethyl alcohol seems to be normal, while in methyl alcohol it seems to be associated with one or two molecules of the solvent."¹ This would account for the abnormally large value of benzil's viscosity constant in methyl alcohol (it is not only much larger than that of benzil in ethyl alcohol, but also than that of urea in either of the alcohols), for the more a solute combines with the solvent the greater is this constant. This is shown by its large value in the lithium chloride solutions. In the potassium iodide solutions the value is smaller, but still considerably greater than in the non-solvated urea solutions. The vapor-pressure constant varies in the same order with the solvation of the solute, but to a much less degree. There is therefore only the most general sort of a parallelism between the two constants.

The values of these constants at other temperatures than 15° illustrates the effect of change of temperature upon them. As is well known, Babo's law states that the relative lowering of the vapor pressure of a solution at any given concentration is independent of the temperature, and this has recently been confirmed by Price, that is the expression $p - p'/pc$ would be constant at different temperatures, which is seen to be true. As to the viscosity constant, it shows but little variation with the temperature. As far as these results are concerned it is apparently constant for moderate changes of temperature. However, the data here are too meagre to warrant a sweeping statement.

In a recent paper by Jones and associates,² the opinion is expressed that the negative viscosity exhibited by some salts of caesium, rubidium, potassium and ammonium in certain solvents depends, among other things, on the association of the solvent. No negative viscosities were found for any of the solutions of these salts in formamid, and they therefore conclude that this is due to a certain extent to the high association of this solvent. It is, however, so far as has been investigated, only in water and glycerol of the pure solvents that these salts yield negative viscosities. No such negative viscosities have been observed in pure

¹ Tower and Germann, *loc. cit.*, p. 2456.

² *Pub. Carnegie Inst.*, 230, p. 36.

methyl or ethyl alcohol nor in acetone. The association factors of these liquids are

Formamid,	6.18	Ethyl alcohol,	2.74
Water,	3.81	Glycerol,	1.80
Methyl alcohol,	3.43	Acetone,	1.26

The phenomenon of negative viscosity in these solvents has nothing apparently in common with the order of these numbers, and until a great deal more data are at hand it will be impossible to show what the influence of the solvent is upon it.

With regard to the nature of the solute, the theory of Jones and Veazey¹ seems plausible, that is, that it is due to the large molecular volume of this component of the solution.

In the paper to which reference has just been made a number of viscosity measurements of salts in formamid at 15°, 25° and 35° are reported.² Unfortunately, the concentrations are expressed in volume normal terms and no densities are given, so that direct comparison with the results of this paper can not be made. However, values of the expression $\eta' - \eta/\eta c'$ in which c' is the volume normal concentration, can be calculated; and such values, though not exactly proportional to the values of the expression used above, will enable one to form some idea of its constancy. I have made this calculation for a number of salts at different temperatures, and find the numbers so obtained to be approximately constant for the same salt and to be smaller for salts like CsNO_3 and $\text{N}(\text{C}_2\text{H}_5)_4\text{I}$, which are not solvated, than for salts like NaI and LiNO_3 , which probably do combine more or less with the molecules of the solvent. At different temperatures the values are usually a little less at 35° than at 15°, but this is not always the case. In these formamid solutions the viscosity was determined only at three concentrations (sometimes only two), hence the data are rather insufficient for any broad generalization. Furthermore, all of the solutes employed were electrolytes. Simpler relations might be found to hold if non-electrolytes were used. Additional information regarding the points discussed in this paper could probably be obtained by measuring the viscosity of solutions in a non-associated solvent. The author expects to take up such an investigation at an early date.

Summary.

(1) The viscosity of very pure samples of methyl and ethyl alcohols has been determined, and also that of mixtures of these substances with small proportions of water.

(2) The viscosity of solutions of a number of typical solutes in these alcohols has been measured, and the value of the expression $\eta' - \eta/\eta c$

¹ *Am. Chem. J.*, 37, 405 (1907).

² Jones and associates, *Pub. Carnegie Inst.*, 230, p. 16.

has been compared with that of $p - p'/pc$, obtained from former vapor-pressure determinations.

(3) This "viscosity constant" increases with the solvation of the solute, and for the solutions here investigated seems to be almost independent of changes of temperature.

(4) So-called "negative viscosity" is discussed in the light of the results here obtained and also in the light of those obtained by Jones and associates with solutions in formamid and in other solvents.

CLEVELAND, OHIO.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 261.]

THE PROPERTIES OF MIXED LIQUIDS. II. PHENOL-WATER AND TRIETHYLAMINE-WATER MIXTURES.

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The object of this paper is to report the results of the study of two typical, so-called, "mutually soluble" liquid mixtures in a large number of concentrations, and at temperatures lying both above and below the critical solution point, not only from the point of view of surface tension, but also of some other physical properties.

The tip used to determine the surface tension, by aid of the drop-weight method, was standardized¹ by the use of both benzene and water, with the following result, each drop-weight value being the mean of at least three results agreeing to within a few hundredths of one per cent.:

TABLE I.—STANDARDIZATION OF TIP.

Liquid.	t.	Wt. 1 drop. (Mg.). w.	Surface tension (dynes). γ .	Constant (= γ/w).
Benzene.....	30°	28.352	26.625	0.9391
Water.....	30°	75.680	71.033	0.9386

Average..... 0.9389

To find the surface tension of any liquid in dynes per centimeter, from the drop weight in milligrams, at the same temperature, from this tip, we have, then,

$$\gamma_{l,t} = 0.9389 \times w_{l,t}.$$

And since the specific cohesion (a^s) is related to surface tension, through the density, by the equation $a^s_i = 2\gamma_i/9.80 d_i$, we have, substituting for γ , its value in terms of w ,

$$a^s_{l,t} = 2 \times 0.9389 \times w_{l,t}/9.80 d_{l,t} = 0.1916 \times w_{l,t}/d_{l,t},$$

so that from the drop weight and the density we can also calculate the value of the specific cohesion for any liquid, at any temperature.

¹ See Morgan, THIS JOURNAL, 37, 1462 (1915).

From the value of the constant, 0.9389, the mean diameter of this tip is calculated¹ to be approximately 5.35 mm.

The sample of phenol used as a basis for this work was prepared especially for us² and was of a high order of purity. So much difficulty had been experienced in the past, however, in obtaining this substance in the pure state, considering the melting point as a criterion, that this original sample was first redistilled three times *in vacuo*, before the final recrystallization was made.

The melting point of the product so obtained was determined, with both a rising as well as a falling column, by aid of a certified thermometer; the solid and liquid phases, when stirred continuously, remaining in equilibrium for more than three hours at a constant temperature of $39.70^\circ \pm 0.02$. This value agrees very satisfactorily with the mean of the determinations of Ladenberg,³ 39.5° ; Guye and Tsakalatos,⁴ 39.5° ; Eykman,⁵ 39.6° ; Paterno and Ampola,⁶ 39.6° ; Riesenfeld,⁷ 39.8° ; and Block,⁸ 39.9° . As variations from this value by as much as from 7–13% are found by other observers,⁹ this property should be an excellent test of purity, for it is hardly possible that any other could be as sensitive.

For use in calculating the values of specific cohesion from those of surface tension (or drop weight), careful determinations of the density of the pure phenol were made at various temperatures, employing an Ostwald-Sprengel pyknometer with stoppered limbs. The results of these measurements are given in Table II.

TABLE II.—DENSITY OF PURE PHENOL.

<i>t</i>	40°	45°	50°	55°	60°	66°
<i>d</i>	1.05794	1.05366	1.04936	1.04508	1.04077	1.03532

Application of the method of least squares to these results leads to the following linear relationship between density and temperature:

$$d_t = 1.09226 - 0.000858 t,$$

which between 40° and 60° represents the experimental results to practically the fifth place of decimals.

Just as with the melting point, the densities of phenol, as determined by other investigators, vary widely among themselves, but naturally to no such extent as in the former case. The above results agree most

¹ See Morgan, *Loc. cit.*

² Prepared by the Hoffman and Kropff Chemical Company.

³ *Ber.*, 43, 202 (1910).

⁴ *J. chim. phys.*, 8, 340 (1910).

⁵ *Z. physik. Chem.*, 4, 502 (1889).

⁶ *Gazz. chim.*, 27, 481 (1897).

⁷ *Z. physik. Chem.*, 41, 1350 (1902).

⁸ *Ibid.*, 78, 397 (1912).

⁹ $34-35^\circ$ to 42.4° .

closely with those of Worley, Thole, Hewitt and Winmill, Bolle and Guye, and Ramsay and Aston, which were taken from Kopp,¹ the difference in few cases being larger than 0.1%, which is to be considered as negligible in the calculation of specific cohesion from the surface tension.

The values of surface tension, specific cohesion, and the density used to obtain the latter from the former, as well as the γ and a^2 values given by interpolation formulas, are presented in Table III, at the various temperatures studied. Each result here is from an average of at least three measurements of drop weight, no one deviating from another by more than a few hundredths of one per cent.

TABLE III.

<i>t</i> .	γ ($= 0.9389 \text{ w} \rho$).	γ (calc.).	<i>d</i> .	a^2 (from γ and d).	a^2 (calc.).
23	39.22	39.28	1.0725	7.46	7.48
30	38.56	38.54	1.0665	7.38	7.38
32	38.35	38.33	1.0658	7.34	7.35
34	38.13	38.12	1.0631	7.32	7.32
36	37.92	37.91	1.0614	7.29	7.29
38	37.68	37.70	1.0597	7.26	7.26
41	37.43	37.38	1.0571	7.23	7.22
45	36.99	36.96	1.0537	7.16	7.16
49	36.57	36.54	1.0503	7.11	7.10
55	35.90	35.91	1.0451	7.01	7.01
60	35.41	35.38	1.0408	6.94	6.94
62	35.12	35.17	1.0391	6.90	6.91
63	34.76	34.75	1.0353	6.85	6.85

Columns 2 and 3, and 5 and 6, agreeing as closely as they do, prove the interpolation formulas derived to represent the experimental results with considerable accuracy. These equations are

$$\left. \begin{aligned} \gamma_t &= 41.701 - 0.1053t \\ a_t^2 &= 7.810 - 0.0145t \end{aligned} \right\} t \text{ from } 23^\circ \text{ to } 63^\circ.$$

A comparison of the values of γ and a^2 interpolated or extrapolated from these equations, with those found directly by other observers, by the capillary rise method, at their temperatures, is made in Table IV.

These results are also presented in graphical form, as respects γ , in Fig. 1, which also includes the results of Bolle and Guye,² uniformly higher than all others by the same method (capillary rise); and those of Feustel,³ by the air bubbling method, very considerably higher than the others, but of about the same temperature coefficient.

With respect to the Feustel results, it may be said that they are uniformly high for all other liquids, when compared to those obtained by capillary rise. Assuming that the method of Feustel is a correct *relative*

¹ *Ann.*, 95, 312 (1855).

² *J. chim. phys.*, 3, 38 (1905).

³ *Ann. Phys.*, 16, 61 (1905).

one, and standardizing it with benzene as we do in the drop-weight method, the results for phenol, and also for several other liquids which

SURFACE TENSION OF PHENOL

have been studied by others, are found to be reduced to the same order as those of the others. Even relatively however, judged by the results of the surface tension of benzene, it can hardly be considered as an accurate method so far as reproducibility of result is concerned, for with that liquid large differences in value (0.1 dyne) appear at temperatures only 0.1° apart, the higher temperature in fact leading to the higher result (*viz.*, at 20.8° and 20.9°, and at 57.1° and 57.2°, at which the γ values

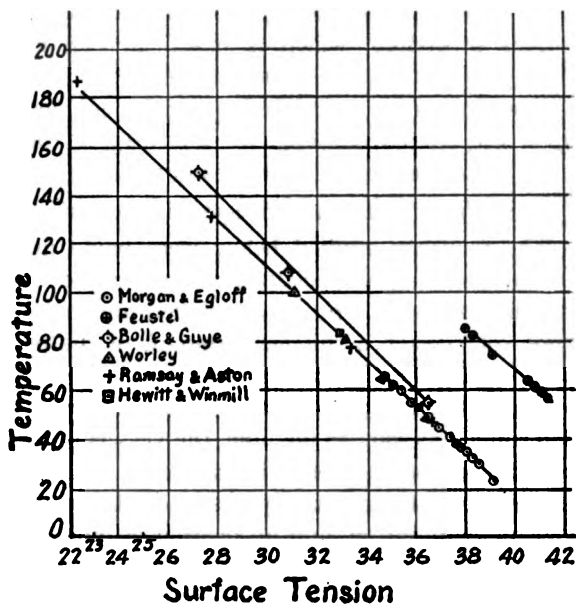


Fig. 1.

as he gives them are, respectively, 30.21, 30.31, 25.02 and 25.11 dynes).

TABLE IV.—A COMPARISON OF RESULTS.

t.	Surface tension, γ .				Specific cohesion, a^2 .			
	R. & A. ¹	H. & W. ²	W. ³	M. & E. (calc.).	R. & A.	H. & W.	W.	M. & E. (calc.).
46.0	36.81	36.86	7.15	7.14
49.0	36.54	36.54	7.09	7.10
53.3	...	36.17	...	36.09	..	7.07	..	7.04
66.0	34.73	34.75	6.81	6.85
78.0	33.32	33.49 ⁴	6.71	6.69 ⁴
81.0	33.16	33.17 ⁴	6.59	6.64 ⁴
83.0	...	32.95	...	32.96 ⁴	..	6.60	..	6.61 ⁴
100.0	31.10	31.17 ⁴	6.26	6.36 ⁴
131.7	27.90	27.83 ⁴	5.88	5.90 ⁴
184.0	22.39	22.33 ⁴	4.98	5.14 ⁴

It will be seen from the above that the tip employed in this work, when

¹ Ramsay and Aston, *J. Chem. Soc.*, 65, 168 (1894).

² Hewitt and Winmill, *Ibid.*, 91, 446 (1907).

³ Worley, *Ibid.*, 105, 267 (1914).

⁴ Extrapolated above last temperature, 63°. The extrapolation in the case of a^2 is really a double one, *i. e.*, of γ , and also of d , which could account for the greater discrepancy in some values of a^2 than of γ , where but the one factor is extrapolated.

standardized by aid of the universally accepted value of the surface tension of water; also gives results for the surface tension of phenol which are in very excellent agreement with those of other observers; the values of Bolle and Guye being excluded here, since they are not in accord with the three other observers using the same method.

This procedure, which is practically an identical standardization of the tip from accepted values of the surface tension of the liquids forming the two extremes, and differing widely, enables us to lay very great stress upon the results obtained for mixtures of the two liquids, which in all cases lie between these extremes in value.

Surface Tension and Specific Cohesion of Water Mixtures.

The mixtures studied below were made up in the following manner, the water being a specially purified sample which was also employed in standardizing the tip: To a weighed amount of the one constituent in a "non-sol" vessel, a sufficient amount of the other was added to give the approximate concentration desired, the actual weight being found by weighing the stoppered vessel. The drop weights in each case were then determined as soon as possible, the vessels being kept in darkness to avoid possible decomposition. Precautions were also taken in transferring the solutions to the supply vessel of the apparatus, to minimize possible loss by evaporation, and absorption of moisture or other impurities from the air, the liquid being cooled to a low temperature just before the transfer. As the whole operation required less than a minute, any change in concentration taking place was negligible.

The values of γ and a^2 found at the various concentrations and temperatures studied, together with the density values¹ employed to calculate the one from the other are given in Table V.

TABLE V.—SURFACE TENSION AND SPECIFIC COHESION OF PHENOL-WATER MIXTURES.

% = grams phenol per 100 g. of mixture.								
% = 0.			% = 0.534.			% = 0.770.		
<i>t.</i>	γ .	a^2 .	γ .	<i>d.</i>	a^2 .	γ .	<i>d.</i>	a^2 .
0°	75.87	15.49	68.23	64.77
20	72.69	14.87	66.13	1.0010	13.50	63.23	1.0010	12.90
30	71.03	14.57	65.19	0.9974	13.32	62.51	0.9986	12.75
35	70.19	14.42	64.77	0.9965	13.27	62.14	0.9976	12.68
40	69.33	14.28	64.30	0.9955	13.20	61.83	0.9968	12.65
45	68.47	14.13	63.79	0.9934	13.13	61.40	0.9936	12.60
50	67.59	13.98	63.27	0.9897	13.06	60.99	0.9905	12.57
55	66.69	13.83	62.80	0.9862	12.98	60.64	0.9882	12.52
60	65.80	13.67	62.30	0.9827	12.92	60.27	0.9862	12.48
65	64.88	13.52	61.82	0.9792	12.85	59.89	0.9841	12.43

¹ These densities are found from interpolation formulas derived from the results of Worley (*l. c.*) for concentrations from 0.5 to 6.25%, and from Friedlander (*Z. physik. Chem.*, 38, 385 (1901)), for those from 9.54 to 100%.

TABLE V (Continued).

% = 0.970.				% = 1.47.			% = 3.48.		
t.	γ .	d.	σ .	γ .	d.	σ .	γ .	d.	σ .
0°	62.31
20	61.02	1.0010	12.46
30	60.27	0.9975	12.36	36.23	1.0000	11.49	46.11	1.0000	9.40
35	60.08	0.9970	12.28	56.08	0.9984	11.46	46.00	0.9986	9.38
40	59.74	0.9965	12.23	55.89	0.9974	11.43	45.91	0.9970	9.36
45	59.44	0.9938	12.20	55.68	0.9954	11.40	45.85	0.9952	9.34
50	59.15	0.9911	12.16	55.44	0.9936	11.38	45.76	0.9940	9.32
55	58.80	0.9904	12.12	55.25	0.9918	11.35	45.65	0.9923	9.30
60	58.47	0.9897	12.05	55.03	0.9901	11.32	45.57	0.9907	9.28
65	58.16	0.9890	11.98	54.78	0.9884	11.30	45.48	0.9890	9.26
% = 4.53.				% = 8.74.			% = 58.6.		
25
30	43.14	1.0012	8.78
35	43.07	1.0006	8.76	37.22	1.0016	7.63
40	42.95	1.0000	8.75	37.09	0.9994	7.57
45	42.82	0.9978	8.73	36.89	0.9975	7.53
50	42.67	0.9955	8.70	36.72	0.9956	7.50
55	42.54	0.9937	8.68	36.53	0.9940	7.47
60	42.36	0.9920	8.66	36.35	0.9925	7.43	35.23
65	42.28	0.9903	8.64	36.11	0.9910	7.39	34.96
% = 65.45.				% = 70.40.			% = 74.00.		
30	38.09	1.0445	7.44	38.22	1.0469	7.42
35	37.72	1.0407	7.40	37.83	1.0447	7.40
40	37.33	1.0369	7.32	37.41	1.0412	7.35
45	36.96	1.0331	7.25	36.99	1.0377	7.28
50	36.23	1.0244	7.23	36.53	1.0294	7.22	36.59	1.0343	7.22
55	35.93	1.0203	7.17	36.15	1.0253	7.20	36.19	1.0301	7.17
60	35.55	1.0162	7.13	35.74	1.0212	7.15	35.77	1.0260	7.13
65	35.23	1.0122	7.10	35.36	1.0171	7.08	35.38	1.0219	7.09
% = 76.60.				% = 100 pure phenol.					
t.	γ .	d.	σ .	t.	γ (calc.).	σ (calc.).			
30	38.29	1.0482	7.45	0°	41.70	7.81			
35	37.89	1.0452	7.40	20	39.59	7.62			
40	37.50	1.0423	7.34	30	38.54	7.38			
45	37.08	1.0391	7.28	35	38.02	7.29			
50	39.65	1.0360	7.22	40	37.49	7.23			
55	36.24	1.0322	7.15	45	36.96	7.16			
60	35.83	1.0285	7.13	50	36.44	7.08			
65	35.44	1.0205	7.08	55	35.91	7.01			
				60	35.38	6.94			
				65	34.86	6.87			

The few results for the surface tension of weak water solutions of phenol given by Worley, seem to accord very satisfactorily with those interpolated, from our results given above, to his concentrations and temperatures. Naturally, the deviations here are much more considerable than in the case of pure phenol, as in fact we should expect, when the enormous

percentage change in the value of γ , due to a very small change in the concentration in solutions of just this order of concentration, is considered.

The Surface Tension of Triethylamine-Water Mixtures.

The sample of triethylamine employed here was originally of a very high order of purity, and just before being used was distilled over completely at a fixed temperature *in vacuo*.

Unfortunately, it has not been possible to calculate the values of specific cohesion (a^2) either for the pure liquid, or for its water solutions, for the densities were not determined at the time, and none can now be found in the literature.

The advantage of this liquid, when mixed with water, over phenol, is that it enabled us to extend the investigation to a point a number of degrees removed from the critical solution temperature, *on the completely miscible side*, which could not be done in the case of phenol. For, in the triethylamine case, the area of complete miscibility lies *below* a certain maximum temperature, while with phenol it lies *above* a certain minimum temperature. On the other hand, it was possible with phenol to attain a point considerably removed from the point of existence of two layers, and on the miscible side, so that a fairly complete general survey of all possible conditions is obtained from a consideration of the two systems.

The results for the surface tension of triethylamine-water mixtures are given in Table VI.

TABLE VI.—THE SURFACE TENSION OF TRIETHYLAMINE-WATER MIXTURES.

% = grams triethylamine to 100 grams of mixture.						
t.	% = 0. γ.	% = 0.50. γ.	% = 1.00. γ.	% = 2.10. γ.	% = 2.44. γ.	% = 4.79. γ.
0°	75.87	58.21	52.49	46.07	...	39.61
19.2	72.82	53.23	47.42	40.25	38.71	31.78
30.0	71.03	51.47	45.01	37.39	35.96	27.18
t.	% = 10.00. γ.	% = 50.50. γ.	% = 75.38. γ.	% = 94.86. γ.	% = 100. γ.	
0°	31.33	25.25	23.94	22.64	22.31	
19.2	24.40	21.73	21.50	20.67	20.53	
30.0	19.56	...	

Discussion of Results.

Up to the present, liquids which mutually dissolve to a limited extent at some one temperature, and which in some cases ultimately mix in all proportions, have been generally distinguished, using a physical property as a criterion, only by the fact that the vapor pressures exhibited by the two constituent layers are identical.¹ But when we consider either layer alone, after its removal from the system, or the system itself after the point of complete miscibility has been passed, even the vapor pressure does not enable us to distinguish it from any other type of liquid mixture.

¹ Konowalow, *Wied. Ann.*, 14, 219 (1881).

By that criterion, then, it has passed from the one type of mixture to another, just as it has visually.

The consideration of the property-composition curves obtained from the above results (see Figs. 2 and 3), for such typical systems of this class as phenol and water, or triethylamine and water,¹ however, shows

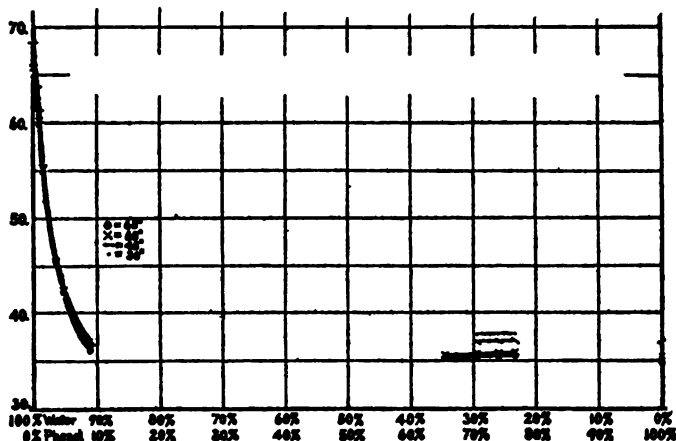


Fig. 2.—Surface tension-composition. Phenol-water.

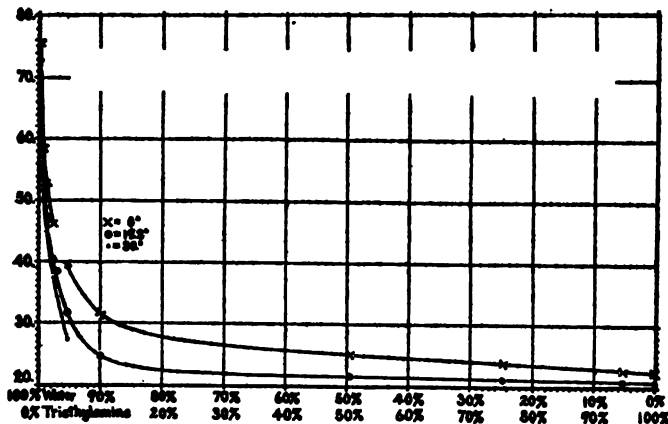


Fig. 3.—Surface tension-composition. Triethylamine-water.

¹ A curve similar to the γ -curves above has already been given by Antonow (*J. chim. phys.*, 5, 371 (1907)) for isobutyric acid-water mixtures, on the basis of a few capillary rise results in the more concentrated solutions. The rapid fall in the surface tension of water, due to the addition of certain other substances, has also already been noted by Whatmough (*Z. physik. Chem.*, 39, 129 (1901), Drucker (*Ibid.*, 52, 649 (1905)), Morgan and Neidle (*THIS JOURNAL*, 35, 1860 (1913)), Worley (*Loc. cit.*) and others; but no complete or general study of such systems has ever been attempted up to the present.

The α^2 -composition curve is so similar to that for γ that it is not necessary to reproduce it here.

that it is possible, with both surface tension and specific cohesion as the physical property selected, to go much farther in the characterization of such systems, not only when in two layers, but also for the one segregated layer, and even for the entire, homogeneous, system up to (or down to) a point considerably removed from the temperatures of complete miscibility.

From these property-composition curves, which certainly differ widely in form from those obtained for either γ or a^2 for any other type of liquid mixture, or from any other property-composition curve, it is to be noted, *first*, and this is apparently characteristic for all such systems, that the liquid of larger surface tension has its value enormously decreased by even small additions of the other liquid. The liquid of the smaller surface tension, on the contrary, is either infinitesimally changed, as far as its property-value is concerned, by a small addition of the other liquid, and then exhibits a constant property-value, independent of the change in concentration, even though this be large (phenol); or, there is a steady, though very small, change in the property-value with changing concentration (triethylamine). In all cases, however, the depression of the property-value of the liquid with the larger surface tension, due to the addition of the other liquid, is such that when the saturation point of the aqueous layer is reached, the property-value has been depressed to a value but slightly removed from the surface tension of the other, pure, liquid.

The steepness of the curve showing the effect, on the surface tension of water, of the addition of the liquid possessing the smaller value, will be seen from the above to depend mainly upon the magnitude of the amount of the second liquid possible in the aqueous layer, and the γ values of water and the other constituent at that temperature. Granting, for example, that two liquids, each forming a two-layer system with water, have identical surface tensions, the one being soluble to 1% and the other to 10% in the aqueous layer, it is evident that the general trend of the γ -composition curve for the addition of the first liquid to water will be steeper than that for the second to water, for in both cases the surface tension of water will have to be depressed to practically the same value, within a few per cent. at most; the one through a distance on the axis of abscissas equal to 1, the other distributed through an interval of 10. If the effect of concentration upon the surface tension were uniform, it would be possible thus to predict, with some degree of accuracy, the actual curve that would be found; and even as it is, this would be possible on the small scale of the curves. The numerical results, however, show this to depend, perhaps, somewhat upon the nature of the liquid—at least we can go no farther, at present.

With phenol-water mixtures, it was not possible to work at a tempera-

ture above the critical solution point. For triethylamine-water mixtures, however, sets of results are given at 0° , about 18.5° on the miscible side, and at 30° about 11.5 on the immiscible side of the critical solution point. The farther a system is removed from its critical point on the immiscible side, the more the above properties are accentuated in every respect. The more it is removed from that point, on the miscible side, the smaller is the effect of the second liquid on the water, and the greater the effect of the water upon it—in other words, the more the system approaches what is probably the most common type of property-composition curve for the surface tension of liquid mixtures.

The results show apparently that phenol reacts differently when water is added to it in small quantities at 60° and 65° from the way it does at 30° and 45° ; for in the latter case the pure phenol has a slightly higher value, and in the former a slightly lower value, than the system produced; the values of γ for the phenol solutions of water being equally independent, however, of changes in concentration through the range investigated.

When the above, evident, properties of such liquid systems, from the point of view of surface tension or specific cohesion, are considered in connection with the curves showing the variation in the deviation of the observed results of γ or α^2 (from those calculated from the law of mixtures)¹ with the percentage composition, a plausible explanation of the generally observed fact of a large change in the surface tension, due to a small addition of a substance to water is offered. Denison² has shown in this connection and from theoretical reasoning that, when a compound is formed by the chemical interaction of the constituents of a mixture, the maximum deviation of a physical property of that system from the value calculated from the law of mixtures, must appear at that composition of the liquid system which corresponds to the composition of the substance found.

In Figs. 4, 5, 6, 7, and 8 are presented deviation curves for γ and α^2 from the above results, as well as those for density and viscosity for phenol-water mixtures,³ and that for γ from our results for triethylamine and water. It is plain that the maximum deviation, as far as the γ and α^2 values are concerned, lies at a composition equal to 8.74 g. of phenol in 100 g. of the mixture, and that the corresponding point for triethylamine and water lies at a 10% concentration. The density and viscosity deviation curves at least enable us to fix a maximum for phenol-water mixtures

¹ See Morgan, *THIS JOURNAL*, 38, 555-568 (1916).

² *Trans. Faraday Soc.*, 8, 20 and 35 (1912).

³ These values for viscosity were obtained from the work of Friedlander (*Z. physik. Chem.*, 68, 32 (1909), and Scarpa (*Cim.*, 6, 277 (1904))), the values for density being from the same source as those above.

somewhere between 5 and 10%, but the data are not sufficient in this region to settle the point more definitely. These values, however, can be considered, as far as they go, as nothing if not confirmatory of the surface tension and specific cohesion maxima. Taking the maximum deviation for phenol-water systems at 8.74%, and that for triethylamine-

Fig. 4 (65°).

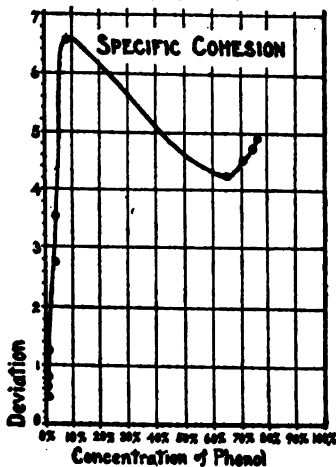


Fig. 5 (65°).

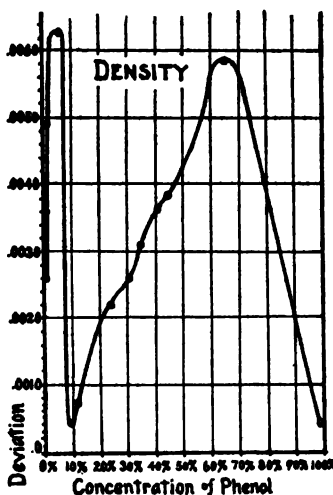
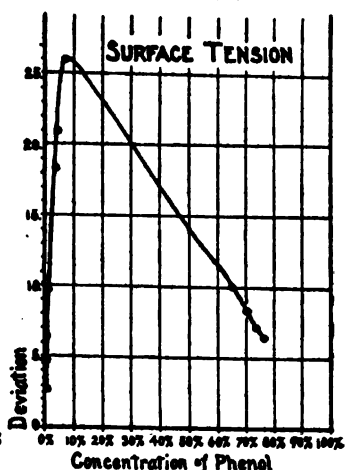


Fig. 6 (70°).

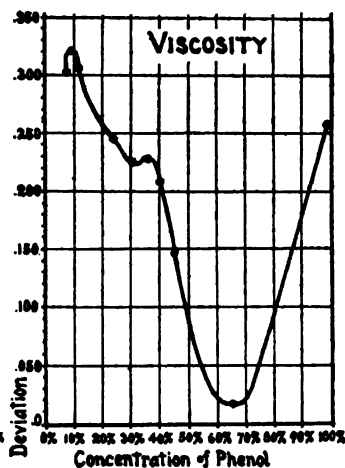


Fig. 7 (70°).

water mixtures as 10%, the temperature not altering at all the concentration at which the maximum is exhibited, we find the compounds formed in the two cases are, respectively: $C_6H_5OH.55H_2O$ and $(C_2H_5)_3N.50H_2O$.

Granting the correctness then, of Denison's method, and the consequent truth of the existence in such systems of chemical compounds, we

see that the first addition to water of any liquid, which is mutually soluble in it, would result in the formation of the compound, and the lowering of the surface tension. Further additions, would then increase the amount of the compound present, with the consequent increase in the depression of the surface tension of the water layer, or what will ultimately be that, until when it is formed to the maximum extent, and all the water is so combined, the surface tension of the water is reduced to nearly that value for the other liquid itself. From the property-composition curves it is clear that the influence of this compound upon the surface tension of the other liquid, when dissolved in it, can be but small in any case.

We have made no attempt in this work to study the surface tensions of the two constituent, mutually saturated, layers of such systems when in equilibrium, feeling that a general survey of the same concentrations at various temperatures more important as a *first* step than the employment of a different concentration for each temperature.¹ From our

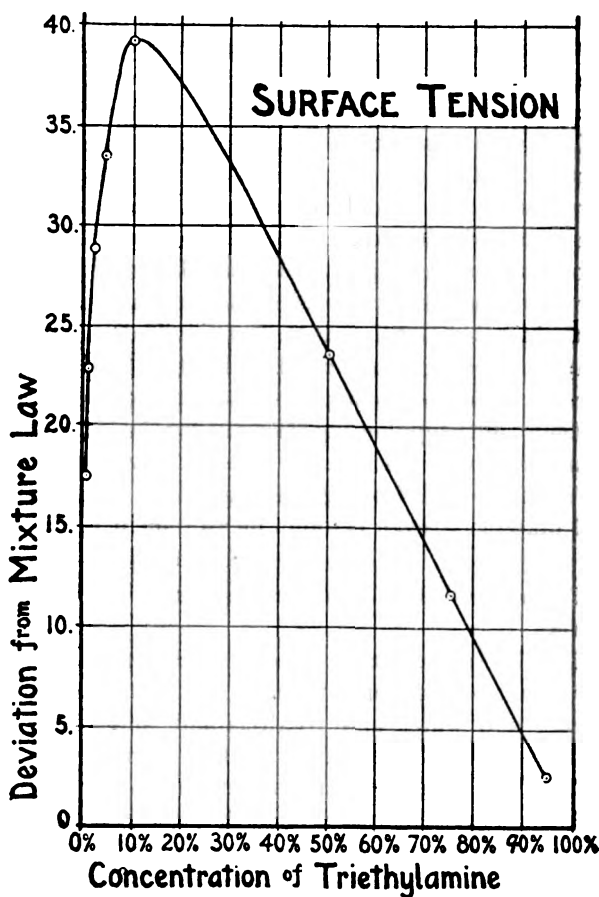


Fig. 8.

results, and the above reasoning, however, it would seem that the water layer consists simply of the compound formed, while the other layer is probably a solution of this compound in the second liquid, affecting its surface tension in the way shown in the curves—the critical solution point

¹ The question as to the surface tensions values of two co-existing layers, mutually saturated, at many temperatures, for a number of such systems is now being investigated in this laboratory and will be reported upon in the near future.

being the temperature at which the compound is soluble in the other liquid in all proportions.

Density and viscosity both show by their deviations the existence of other compounds of phenol and water, which do not appear to be possible of indication by either surface tension or specific cohesion. These are at 36% for viscosity (a faint maximum), and at 65% by density, which would correspond to the formulas $C_6H_5OH \cdot 9H_2O$ and $C_6H_5OH \cdot 3H_2O$, but the deviations in general are so small and the data so distributed, and so meager at the necessary concentrations, that, it is thought, little emphasis can be laid upon the results obtained.

The very exaggerated effect of a small amount of substance on the surface tension of water has usually been attributed to the effect of adsorption, which would cause the surface of the liquid to become more concentrated with respect to the other substance than the interior. The above reasons for this action, *viz.*, that at complete saturation the water layer *must* show a value of surface tension but little removed from that of the pure second liquid itself, which is dissolving; together with the fact that such curve types handled by the Denison deviation method *must* always indicate a compound at the composition of saturation, while perhaps not supplanting the theory based upon adsorption, at least would deserve a place beside it, especially as it has the advantage perhaps of enabling one from general grounds to predict approximately what will take place, even before a measurement is made.

Summary.

The results of this investigation may be very briefly summarized as follows:

I. The surface tensions have been found by the drop-weight method for a number of concentrations of the typical mutually soluble liquids, phenol and water and triethylamine and water, at temperatures both above and below the critical solution point.

II. The property-composition curves for such systems are typical, and characterized by the fact that the constituent of the lower surface tension depresses that of the other to such an extent that the maximum amount soluble in the water layer reduces the surface tension of this to a value differing but slightly from that of the other constituent, when pure. The smaller the amount necessary to saturate the water layer, the greater the effect will have to be, *i. e.*, the steeper the curve must be in all cases when the surface tensions of the second liquid are identical. On the other hand, the effect of the liquid of the larger surface tension upon that of the other is exceedingly slight, and may be independent of the concentration, or vary very slightly with it—according to the nature of the second liquid, perhaps.

III. Using the deviation of property-composition curves as a criterion

as to the possibility of a chemical combination of the constituents of the mixture, both surface tension and specific cohesion show a distinct maximum in the case of phenol at 8.74% phenol, indicating a compound of the formula $C_6H_5OH.55H_2O$, while triethylamine-water mixtures lead to a maximum at 10%, or $(C_2H_5)_3N.50H_2O$. Both density and viscosity for phenol and water, using results from the literature, confirm the above value.

The water layer of such systems must then be considered as transformed completely into a compound, the other layer being the second pure liquid containing the compound in solution, and having its surface tension but little affected thereby. The critical solution point can only be, then, the point at which the compound is completely miscible in the second liquid. As the coexisting layers of such systems in general are now being studied, the further discussion of these points must be postponed.

IV. A theory is presented which at any rate can serve as an alternative to the usual adsorption theory of the exaggerated effect upon the surface tension of water by the addition to it of other liquids.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE MEMORIAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF CADMIUM.

[FOURTH PAPER.]

THE ELECTROLYTIC DETERMINATION OF CADMIUM IN CADMIUM BROMIDE.

BY GREGORY PAUL BAXTER, MERRITT ROY GROBE, AND MINNER LOUIS HARTMANN.

Received January 12, 1916.

Recently the atomic weight of cadmium has been redetermined by Baxter and Hartmann¹ in this laboratory by the electrolytic analysis of cadmium chloride. By using a glass electrolytic cell of special design it was found possible to deposit the metal in a mercury cathode directly from the solution of the salt. The results of this work fully substantiate the value for the atomic weight of cadmium previously established in the Harvard laboratory by Baxter, Hines, and Frevert² through comparison of the chloride and bromide of cadmium with silver. Both methods yielded the result 112.417 ($Ag = 107.880$). The electrolytic analysis of cadmium chloride was instigated by investigations by Perdue and Hulett,³ Laird and Hulett,⁴ and Quinn and Hulett,⁵ who have recently obtained a considerably lower value,

¹ THIS JOURNAL, 37, 113 (1915); *Z. anorg. Chem.*, 92, 53.

² *Ibid.*, 27, 222 (1905); 28, 770 (1906); *Ibid.*, 44, 158; 49, 415.

³ *J. Phys. Chem.*, 15, 1579 (1911).

⁴ *Trans. Am. Electrochem. Soc.*, 22, 385 (1913).

⁵ *J. Phys. Chem.*, 17, 780 (1913); THIS JOURNAL, 37, 1997 (1915).

112.3, by the electrolytic analysis of cadmium sulfate and cadmium chloride and cadmium bromide, and by the comparison of simultaneous deposits of silver and cadmium. In order to obtain further evidence on the subject, the analysis of cadmium bromide by an electrolytic method similar to that employed by Baxter and Hartmann has been carried out. The results of this work confirm very closely all the earlier work in the Harvard Laboratory. Just as the sum of the percentage of chlorine in cadmium chloride found by Baxter, Hines, and Frevert and the percentage of cadmium found by Baxter and Hartmann is 100.000, so the sum of the percentage of bromine in cadmium bromide found by Baxter, Hines, and Frevert, 58.708, and the percentage of cadmium as determined in the present research, 41.290, is 99.998. It is difficult to imagine more convincing evidence of the accuracy of the two methods of analysis.

Purification of Reagents.

Water, nitric acid, sulfuric acid, alcohol and mercury were purified as described by Baxter and Hartmann.¹ In a few experiments mercury, which had been not only three times distilled in vacuum, but also once at low pressure in a current of air, was used. No difference in the behavior of the two samples could be detected. Bromine was freed from impurities by the processes used by Baxter and Grover,² and from the pure bromine hydrobromic acid gas and its solution were prepared by synthesis with pure electrolytic hydrogen in the same way and with the identical apparatus employed by Baxter and Grover.

Purification of Cadmium Bromide.

Since in the earlier work Baxter and Hartmann found that crystallization of cadmium bromide is a very rapid and convenient method of freeing cadmium from metallic impurities, this method of purification was used in preparing the salt for the present purpose. Nonmetallic impurities, such as silica and organic matter, were eliminated both by crystallization and by fusion of the salt in an atmosphere of nitrogen charged with hydrobromic acid gas.

Sample A was prepared from crude cadmium, containing lead and traces of copper and thallium, by cleansing the metal superficially and dissolving it by treatment with the purest bromine under dilute hydrobromic acid solution in a Jena flask. The excess of bromine was removed by boiling, and after filtration through platinum sponge, the solution was evaporated in a platinum dish to crystallization. The salt was five times recrystallized. Since even then the salt, upon fusion, yielded a small amount of black insoluble matter which has been shown elsewhere³

¹ *Loc. cit.*

² *THIS JOURNAL*, 37, 1029 (1915).

³ Baxter and Hartmann, *Ibid.*, 37, 121 (1915); Baxter and Grover, *Ibid.*, 37, 1040 (1915).

to consist chiefly of carbon and silica, the whole was fused in platinum boats contained in a quartz tube in an atmosphere charged with hydrobromic acid gas, in the fashion described later. The insoluble matter was removed by solution and filtration through platinum sponge and the salt was twice more crystallized in platinum vessels. The product, when fused, yielded little, if any, of the black residue.

In all the crystallizations the salt was centrifugally drained in platinum Gooch crucibles,¹ and the evaporation of the solutions was carried out upon electric stoves, in order to avoid contamination from the products of combustion of illuminating gas. Sample A was used in Analyses 1 and 3.

To prepare Sample B the metal was first transported electrically from an anode of commercial cadmium through an electrolyte of very concentrated cadmium bromide solution to a platinum wire cathode, where it was deposited in the form of a crystalline mass. In this way carbon and other nonmetallic impurities were very largely eliminated. Since, however, it is impossible to wash clean an electrolytic deposit of the nature of that obtained in this process, the precaution was taken of using for the electrolyte cadmium bromide which was free from chloride. As a matter of fact, the electrolyte was prepared from the mother liquors of Sample A. The mass of crystals was washed by decantation as thoroughly as possible by prolonged treatment with pure water, and then was converted into bromide by covering it with very dilute hydrobromic acid solution in a quartz flask, and adding freshly distilled bromine. The resulting solution of bromide was then boiled for several hours in contact with a small amount of the purified metal, in order to precipitate as far as possible the more highly electropositive metals. Next, the solution was filtered through a platinum-sponge crucible, held in a platinum funnel, into a platinum dish, and was evaporated to crystallization. After the product had been once recrystallized from pure water in platinum, it was fused in platinum boats in a quartz tube in an atmosphere of nitrogen highly charged with hydrobromic acid gas. Since the fused salt contained a small amount of the black insoluble material, it was now dissolved in water and the solution was again filtered through platinum sponge. Then the solution was evaporated to crystallization, and the product was three times more recrystallized from the purest water, all in platinum vessels with the utmost care to avoid the introduction of dust. The product was perfectly white, and gave after fusion in an atmosphere containing hydrobromic acid only a trace of the black residue.

In order to find out whether foreign metals had been successfully eliminated, a portion of the salt was dissolved in a minimum amount of water and metal deposited from it upon a platinum cathode as completely as

¹ Baxter, *THIS JOURNAL*, 30, 286 (1908).

possible, with the use of a platinum anode also. The crystals were washed very thoroughly and dried in a vacuum desiccator. Then the metal was fused in a hard glass tube in a current of hydrogen gas, and while still fused drawn up into capillary tubes of hard glass. In order to prevent the metal from sticking to the capillary tube, the inside of the capillary was lightly coated with soot by drawing a luminous flame into the tube. If this is done, the glass is very easily cracked from the metal wire thus formed. The spark spectrum was then produced from these electrodes, and photographed in a Féry quartz spectrograph, in which the range $\lambda 2100$ – $\lambda 6000$ is covered. The spectrum showed no lines other than those usually associated with cadmium, and was identical in every way with the spectrum of the purest material prepared by Baxter and Hartmann.

Sample C of cadmium bromide was prepared in essentially the same manner as Sample B. Sample C was probably purer than any of the others, for upon fusion it yielded least of the black residue, some of the specimens being entirely free from any visible matter of this kind. Sample B was used in Analyses 2 and 4, Sample C in Analyses 5 and 11.

By good fortune a small amount of cadmium bromide remaining from the earlier research by Baxter, Hines and Frevert had been preserved in a dry state in a sealed glass tube. This material is designated in the earlier research, Samples II and III. On fusion in hydrobromic acid this material yielded a small amount of the black residue of carbon and silica, but no more, judging from the appearance and recent experience in this laboratory, than 0.001–0.002%. This is designated Sample D in the table of results. Some of the sulfate from which this bromide had been prepared, also remained. Metal prepared from this sulfate gave a spectrum free from the lines of foreign metals.

Preparation of the Cadmium Bromide for Analysis.

To prepare the cadmium bromide for weighing it was fused in a dry atmosphere charged with pure hydrobromic acid gas. The salt was contained in a quartz boat, and this in turn was placed in a transparent quartz tube, which formed part of a "Bottling apparatus"¹ such as is usually employed in this laboratory for transferring a boat to a weighing bottle without exposure to moisture. The hydrobromic acid gas was prepared by synthesis from pure bromine and hydrogen in the same apparatus and in exactly the same way as in a research upon lead bromide by Baxter and Grover.² In the earlier experiments the fusion atmosphere was prepared by passing pure nitrogen through fuming hydrobromic acid solution, and then, in order to remove moisture, over fused calcium bromide. In many of the final series of experiments the fusion atmos-

¹ Richards and Parker, *Proc. Am. Acad.*, 32, 59 (1896); *Z. anorg. Chem.*, 13, 85.

² THIS JOURNAL, 37, 1035 (1915).

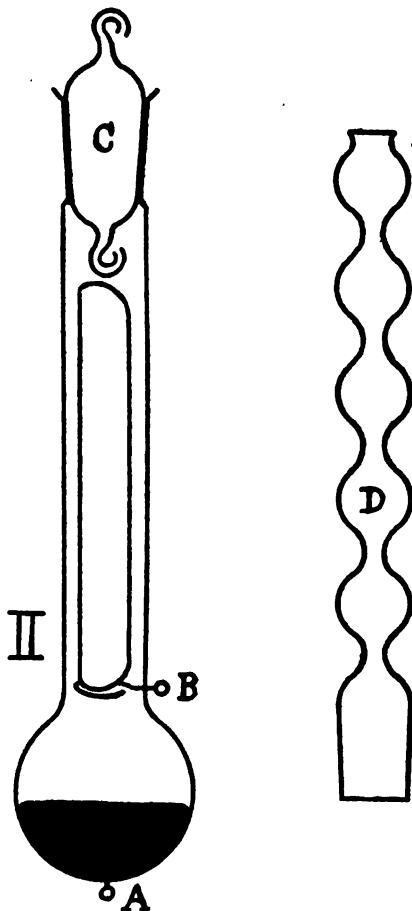
phere consisted of hydrogen which had been charged with hydrobromic acid in the same way. No difference in the appearance or the composition of salt fused in the two atmospheres could be detected.

Previous to fusion the cadmium bromide was freed from a portion of its crystal water in a vacuum desiccator containing fused potassium hydroxide. Then, after the greater part of the residual water had been expelled at a low temperature by heating the salt in the hydrobromic acid atmosphere, the temperature was gradually raised by means of an electrically heated sleeve until the salt was fused. As soon as the salt had solidified, the fusion atmosphere was displaced with pure nitrogen and this finally with pure, dry air,¹ and the boat and contents were transferred to the weighing bottle in which they were to be weighed, without exposure to the outside air.

The quartz boats with their weighing bottles were found to remain unaltered in weight by the treatment during fusion. This confirms earlier experience in this laboratory and elsewhere.

Method of Analysis.

For all the electrolyses a cell of the form II, as shown in the earlier paper by Baxter and Hartmann, was employed. In order that the cell might be subjected as far as possible to the same influences before the initial weighing as before the final weighing, it was carefully cleaned and provided with suitable charge, usually about one hundred grams, of the purest mercury, and the mercury was then made the cathode during the electrolysis of dilute sulfuric acid for several hours. Then the cell was rinsed first with water, then with alcohol. The outside also was cleaned and wiped with a clean, lintless cloth. In order to dry the cell and contents, it was placed in a tubular desiccator containing fused potassium



¹ The air and nitrogen were purified and dried as described by Baxter and Grover, *Loc. cit.*

hydroxide and the pressure was reduced as far as possible with a Geryk oil pump. When the alcohol had evaporated, the cell and its counterpoise were placed in a second vacuum desiccator containing fused potassium hydroxide, and allowed to stand for several hours before being weighed.

Next the quartz boat with its content of cadmium bromide was introduced bodily into the cell and the salt was dissolved in the rinsings of the weighing bottle. The column of bulbs to catch spray formed during electrolysis was inserted and electrolysis was begun, usually with current strength of about one-half ampere. A strong current at the start was found to delay the completion of the electrolysis. The cell was partly immersed in the purest water in order to avoid undue heating during electrolysis. By experiment this water was proved to exert no appreciable solvent effect upon the glass of the cell.

One of the chief difficulties met in the work was the removal of the bromine liberated at the anode, which, owing to its considerable solubility, nearly all dissolved in the bromide solution, and was only slowly eliminated by evaporation into the small volume of gases produced at the electrodes. This dissolved bromine, by its action on the amalgam, greatly retarded the deposition of the cadmium. Various means of hastening the evaporation of the bromine were tried, including the addition of sulfuric acid before electrolysis was begun, varying the current strength and the concentration of the solution, as well as the temperature, but the only one which was at all successful was to cause a stream of very small bubbles of pure electrolytic hydrogen to pass through the electrolyte through a small glass tube which extended nearly to the surface of the mercury. Even with this device a small amount of bromine remained in the solution after electrolysis for eighteen hours. By that time, however, nearly all the cadmium was deposited and it was safe to remove the electrolyte and eliminate all bromine and bromide by conversion to sulfate.

Before doing this the column of bulbs was rinsed into the cell and the current strength was increased to a maximum by applying the full potential of the battery (seventeen volts) across the electrodes. Next the electrolyte was removed by suction as completely as possible, and the amalgam was washed with a few portions of water and left standing under a very dilute solution of sulfuric acid. The electrolyte was transferred to a quartz dish and evaporated with a few drops of distilled sulfuric and nitric acids, until the bromine and nitric acid had been expelled, and the sulfuric acid was fuming. The residue, which amounted to only a few milligrams, was dissolved in water and returned to the cell, and the electrolysis was continued over another period, usually of sixteen hours, with a current strength of between half and one ampere. The electro-

lyte was now replaced with very pure water, the full potential being maintained between the electrodes, and great care being taken not to break the electrolytic circuit. Then the water was removed as completely as possible, and the amalgam was rinsed with two small portions of chilled water which had been saturated with hydrogen, and two small portions of the purest alcohol, the amalgam being rolled round gently so as to bring the surface in thorough contact with each washing portion. The outside of the cell was then carefully cleaned and wiped dry, and the amalgam was freed from alcohol exactly as the mercury originally was treated. In accordance with the earlier experience of Baxter and Hartmann we found the amalgams to remain constant in weight when preserved in vacuum.

The electrolyte and washings were evaporated nearly to dryness in a quartz dish over an electric stove. After transference to a weighed platinum crucible, evaporation was continued at a gradually increasing temperature until finally the sulfuric acid had been expelled. Eventually the residue was heated to very dull redness, before being cooled and weighed. While this residue was always small, in no case was it negligible, and occasionally weighed several milligrams. After being weighed it was in many cases dissolved in very dilute sulfuric acid and the solution tested for cadmium with hydrogen sulfide. Cadmium was always found, usually in amounts corresponding very nearly to the weight of the sulfate. Undoubtedly, however, a small proportion of the residue consisted of sulfates of alkalis extracted from the glass of the cell. Since the residue is always multiplied by the proportion of cadmium in cadmium sulfate, 0.54, before the correction is applied, no serious error could have been introduced in this way. That this is the case is indicated by the fact that the total weight of cadmium computed from amalgam and residue eventually became constant upon repeated electrolysis, while the residue seldom changed in weight materially, and frequently decreased.

In the earlier analyses the percentage of cadmium in the bromide was found to be even higher than corresponds to the atomic weight 112.42. The results for the atomic weight of cadmium varied somewhat, the highest being 112.477 and the lowest 112.387, with an average of 112.43. The amalgams, while not badly rusted, were, however, not quite so bright in appearance as in the earlier electrolyses of cadmium chloride. In Analysis 1, in Table I, in which the initial result was somewhat higher than usual, the experiment was tried of repeatedly dissolving the residue of cadmium sulfate in dilute sulfuric acid, returning it to the cell and continuing the electrolysis for another period of several hours. The result of these experiments was to diminish the total weight of cadmium found in the amalgam and residue by about two milligrams, the change falling chiefly upon the weight of the amalgam. Ultimately, a point was reached

where repeated electrolysis produced no further alteration in the weight of cadmium recovered. These additional electrolyses, besides lowering the total weight of cadmium, also improved the appearance of the amalgam perceptibly, the final product being as bright and silvery in appearance as could be desired. While we are not certain as to the exact cause of this diminution in weight, we are strongly inclined to the belief that it is due to a small amount of mercurous bromide on the surface of the amalgam, which is only gradually reduced to the metallic state by prolonged electrolysis. This mercurous bromide might very well be formed through the action of the free bromine always present during the first stage of the electrolysis. After this experience, in every analysis the residue was dissolved in dilute sulfuric acid, returned to the cell and the electrolysis repeated until the cadmium recovered in the form of amalgam and as sulfate reached a constant minimum value. This required from three to five electrolyses. The ultimate result of this change in procedure was to lower slightly the average percentage of cadmium in the bromide from that obtained in the first series of experiments.

In order to make certain that the final weight of cadmium found in this way is the correct one, two experiments, Analyses 10 and 11, were carried out by converting the bromide completely to sulfate before electrolysis was begun. This is the method employed by Quinn and Hulett for the analysis of cadmium bromide. The boat with the fused salt was transferred to the quartz dish and the salt was dissolved in water. The boat was carefully removed with rinsing, and the solution was slowly evaporated on an electric stove with a slight excess of redistilled sulfuric and nitric acids, until the bromine and excess of nitric acid had been expelled. The greatest pains was taken toward the end of the evaporation to avoid spattering. The residue of cadmium sulfate and sulfuric acid was dissolved in water and the solution quantitatively transferred to the cell and electrolyzed. The amalgam was treated as above preparatory to weighing, and the residual electrolyte was evaporated in quartz and finally in a platinum crucible, and the residue of sulfate was weighed. The residue was dissolved in dilute sulfuric acid, returned to the cell and electrolysis was repeated. In Analysis 10 the change in weight when electrolysis was repeated was 0.01 mg. In Analysis 11 during the first repetition the loss was one milligram, owing apparently to the fact that some undecomposed bromide was left in the sulfate, but in the second repetition a gain of 0.06 mg. occurred. The agreement of the results of these two experiments with those of experiments where the bromide was electrolyzed directly is strong evidence that no serious error affected the latter.

A question raised by the gradual loss in weight of the cadmium amalgam during continued electrolysis of the bromide is whether in the earlier

analyses of cadmium chloride a similar process might not have been under way but not detected. Therefore, in order to determine whether in the analysis of the chloride it is necessary to continue electrolysis to constant weight, several experiments were carried out, in as nearly as possible the same fashion as in the work by Baxter and Hartmann, except that the residue was dissolved, returned to the cell and electrolysis repeated one or more times after the initial weight had been obtained. The material was made from Sample C of cadmium bromide used in the present work by converting it to chloride in a stream of chlorine and hydrochloric acid. The latter process was carried out exactly as described in the earlier paper on the analysis of the chloride.¹ In no one of the three analyses in which electrolysis was repeated could a change in the total weight of cadmium as large as a 0.1 mg. be detected. One analysis in which an obvious loss of material occurred is not given in the table. The final average of the three determinations is essentially the same as that found before. We therefore feel reassured that no difficulty such as was experienced with the bromide could have affected the chloride analyses. It is not surprising to find this to be the case, however, since the free chlorine, being more volatile and less soluble in the electrolyte, is far more rapidly removed during electrolysis than the free bromine.

The weights were standardized to hundredths of a milligram by the substitution method described by Richards.² All weighings were made upon a No. 10 Troemner balance. With the heavier objects, such as the weighing bottle, and the cell containing mercury or amalgam, the balance beam was left down some minutes before making observations in order to allow the slight bending of the beam to occur. A small amount of crude radium bromide was kept in the balance case to prevent the objects weighed from retaining electrostatic charges. The weighing bottle and cell were always compared with counterpoises of very nearly the same shape, size and volume in order to avoid variations from changes in atmospheric conditions.

Vacuum corrections of +0.000086 g. per gram of cadmium bromide and of +0.000152 g. per gram of cadmium chloride were applied, the densities of the weights and the salts being assumed to be 8.3, 5.192 and 4.047, respectively. The vacuum correction of cadmium dissolved in mercury computed in the earlier paper, —0.000016 g., was applied for every apparent gram of dissolved cadmium. In a few analyses the amalgam was so concentrated that a small amount of solid amalgam separated, but not in amount large enough to produce uncertainty in the vacuum correction.

¹ Baxter and Hartmann, *Loc. cit.*, p. 130.

² THIS JOURNAL, 22, 144 (1900).

THE ATOMIC WEIGHT OF CADMIUM.¹Cd:Br₂.

Br = 79.916.

Number of analysis.	Sample of CdBr ₂ .	Wt. of CdBr ₂ in vacuum. Grams.	Wt. of Cd from amalgam in vacuum. Grams.	Wt. of residue from electrolyte. Gram.	Total of Cd in vacuum. Grams.	Ratio Cd: Br ₂ .	Atomic wt. of Cd.
1	A	16.55663	6.83503	0.00133	6.83575	0.703203	112.395
2	B	6.83764	2.82293	0.00090	2.82342	0.703355	112.419
3	A	7.16223	2.95618	0.00144	2.95696	0.703155	112.387
4	B	6.71886	2.77347	0.00124	2.77414	0.703255	112.402
5	C	10.31855	4.26065	0.00087	4.26112	0.703453	112.434
6	C	9.40020	3.88027	0.00213	3.88142	0.703311	112.412
7	C	8.21123	3.38976	0.00115	3.39038	0.703274	112.406
8	C	10.51504	4.33980	0.00323	4.34154	0.703254	112.403
9	C	10.22411	4.22110	0.00087	4.22157	0.703297	112.409
10	C	10.99613	4.53953	0.00112	4.54013	0.703242	112.401
11	C	11.05166	4.56258	0.00109	4.56317	0.703271	112.405
12	D	19.67134	8.12101	0.00266	8.12244	0.703309	112.411
Average,							0.703282 112.407
Total, 127.66362		52.71204	0.703281	112.407	

THE ATOMIC WEIGHT OF CADMIUM.

Cd:Cl₂.

Cl = 35.457.

Number of analysis.	Wt. of CdCl ₂ in vacuum. Grams.	Wt. of Cd from amalgam in vacuum. Grams.	Wt. of residue from electrolyte. Gram.	Total wt. of Cd in vacuum. Grams.	Ratio Cd : Cl ₂ .	Atomic wt. of Cd.
13	6.49746	3.98314	0.00216	3.98430	1.58537	112.425
14	6.62682	4.06323	0.00047	4.06348	1.58523	112.415
15	7.35812	4.51120	0.00084	4.51165	1.58500	112.399
Average,					1.58520	112.413
Total,	20.48240	12.55943	1.58519	112.412

One analysis is omitted from the table of bromide experiments because the stopper blew out of the cell during the drying of the amalgam, and one because of the presence of a relatively large amount of readily volatile solid residue when the electrolyte was evaporated to dryness. The amalgam in Analysis 2 was re-electrolyzed only once, and lost in the process 0.00062 g. This may account for the fact that the result of this experiment is slightly higher than the average. In Analysis 7 constant weight of the cadmium was not secured because of accident to the residue after the third electrolysis. In the second electrolysis the loss in weight was 0.00055 g.; in the third 0.00024 g. It is unlikely, that an appreciable further loss would have occurred. In Analysis 5, a very slight black ring, presumably of mercury sulfide, formed on the glass

¹ Some of the preliminary analyses of cadmium bromide were made by Dr. Hartmann. The final analyses given in the tables were all made by Mr. Grose.

of the cell at the surface of the mercury, during the electrolysis with sulfuric acid.

In connection with the table it is worth noting that if the weight of residue obtained from the electrolyte is entirely neglected, the atomic weight of cadmium becomes 112.37. But this value is surely too low, first, because the residues always contained cadmium and second, because of material dissolved from the cell walls.

The average result, 112.407, confirms all the earlier work in the Harvard Laboratories upon the analysis of the cadmium halides. The average percentage of cadmium in cadmium bromide found here is 41.290, while Baxter, Hines, and Frevert by comparing the same salt with silver found the percentage of bromine to be 58.708. The sum is 99.998%, a satisfactory outcome.

The following table summarizes the work upon the atomic weight of cadmium carried out in the Harvard Laboratories:

	Ratio.	Atomic weight of cadmium.
Baxter and Hines.....	$\text{CdCl}_2:2\text{Ag}:2\text{AgCl}$	112.418
Baxter, Hines and Frevert.....	$\text{CdBr}_2:2\text{Ag}:2\text{AgBr}$	112.417
Baxter and Hartmann.....	$\text{CdCl}_2:\text{Cd}$	112.417
Baxter, Grose and Hartmann.....	$\text{CdBr}_2:\text{Cd}$	112.407
		<hr/>
		Average, 112.415

It is difficult to believe that constant errors could have affected all four series of results to an equal extent.

Summary.

1. A procedure for the direct electrolysis of bromides with the use of a special form of cell and a mercury cathode is described.
2. Further evidence is presented in support of the analyses of cadmium chloride by Baxter and Hartmann.
3. The percentage of cadmium in anhydrous cadmium bromide is found to be 41.290, while Quinn and Hulett found only 41.257%. The former percentage corresponds to an atomic weight of cadmium of 112.407 ($\text{Br} = 79.916$), a value which agrees satisfactorily with the results obtained earlier by Baxter, Hines, and Frevert, and Baxter and Hartmann, 112.417 ($\text{Cl} = 35.457$). The average of the four series of results is 112.415 ($\text{Ag} = 107.880$).

We are greatly indebted to both the Carnegie Institution of Washington and the Elizabeth Thompson Science Fund for very generous assistance in this investigation

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF ZINC. THE ELECTROLYTIC DETERMINATION OF ZINC IN ZINC BROMIDE.

BY GREGORY PAUL BAXTER AND MERRITT ROY GROSE.

Received January 12, 1916.

The success met in the electrolytic estimation of cadmium in cadmium chloride and bromide led to the hope that a similar method might be successfully applied to other elements. In the case of the metallic halides it is thus possible to make a complete analysis, that is, the halogen may be determined by comparison with silver and the metal by electrolytic deposition. Where the sum of the two is essentially 100% the evidence obviously is of the strongest kind that constant error has affected neither method.

The close similarity of cadmium and zinc in properties made it likely that the methods as worked out for cadmium could be applied with little variation to the determination of zinc. Such proved to be the case. We found it possible in the first place to deposit zinc in a mercury cathode very nearly although not quite completely, and that the zinc amalgam could be satisfactorily washed with alcohol and dried without perceptible rusting. The amalgam thus produced does not oxidize at all rapidly, even on exposure to air. The general method of procedure was essentially that described in detail in the preceding paper upon the analysis of cadmium bromide. Weighed amounts of zinc bromide which had been dried by fusion were dissolved in a small amount of water in a glass electrolytic cell, and the metal was deposited as completely as possible in a mercury cathode, the bromine liberated at the anode being swept away by bubbling a slow current of hydrogen through the solution. The electrolyte was then completely freed from bromine and bromide by evaporation with nitric and sulfuric acids, and the residue was returned to the cell for further electrolysis. The amalgam finally was washed with alcohol and dried in a vacuum, while the electrolyte was evaporated and a slight residue of zinc sulfate was weighed. In other experiments the zinc bromide was completely converted to sulfate before electrolysis.

Purification of Materials.

Reagents were purified exactly as described in the previous paper.

Zinc Bromide.—Analysis 1 was made with zinc bromide prepared from commercial zinc by treatment with the purest bromine and purified by many crystallizations. For the other experiments material was purified with greater care as follows: Crude metal was freed from nonmetallic impurities by electrolytic transport from an anode of commercial metal through a concentrated solution of zinc bromide free from chloride to a platinum cathode, where the metal was deposited as a fine crystalline

mass. The crystals were leached as thoroughly as possible by digesting with cold, very pure water for some days, and then were dissolved by treatment with very pure bromine under dilute hydrobromic acid solution in a quartz flask. The solution was digested with an excess of zinc in order to remove more strongly electropositive metals, and after filtration through platinum sponge was evaporated to crystallization, and the product was three times more crystallized from very dilute hydrobromic acid solution in platinum vessels. A portion of the product was used for one analysis (Analysis 2). The remainder was fused in platinum boats in nitrogen charged with hydrobromic acid gas. The fused salt, which contained a very small amount of black material, probably carbon and silica as has been previously shown,¹ was dissolved in water and the solution was filtered through platinum sponge. The solution was then evaporated to crystallization, and the crystals were once recrystallized from very dilute hydrobromic acid solution. In all the crystallizations centrifugal drainage in platinum Gooch crucibles was used. The final product, when fused in an atmosphere containing hydrobromic acid gas, was free from all but the merest traces of black residue.

In order to follow the purity of the product, electrodes were made from the crude zinc, from the electrolytic product, and from the four and six times crystallized salt, and the spark spectra of the electrodes were photographed with a Féry quartz spectrograph. In order to prepare electrodes from the salt, a portion was dissolved in water and the metal was deposited as completely as possible from the solution, using platinum electrodes. The electrolytic deposit was thoroughly washed and dried, fused in an atmosphere of hydrogen in a hard glass tube, and made into electrodes by sucking the melted metal into hard glass capillaries. The crude material contained lead, cadmium and iron. The electrolytic metal was nearly free from iron, but contained the other impurities. The four times crystallized zinc bromide contained the merest traces of cadmium and lead, while in the spectrograms obtained with the final product only the strongest lines of cadmium were barely visible. We estimate the proportion of cadmium in the final product to be less than 0.001%.

To dry the salt for weighing it was first left in an exhausted desiccator over fused sodium hydroxide for some days. Then the crystals, which still contained the greater part of the water of crystallization, were heated gently in a weighed quartz boat in a current of either nitrogen or hydrogen, charged with hydrobromic acid gas by being passed through a fuming solution of the acid gas and dried by means of fused calcium bromide. During this process the boat was contained in a quartz tube which formed part of a "bottling apparatus." As soon as the crystal water had evapo-

¹ Baxter and Hartmann, *THIS JOURNAL*, 37, 121 (1915); Baxter and Grover, *Ibid.*, 37, 1040 (1915).

rated from the salt, the temperature was gradually raised until finally the salt was fused. After being allowed to solidify in the acid gas, the latter was replaced first with pure dry nitrogen and this in turn with pure, dry air. The boat was finally transferred to the weighing bottle in which it originally had been weighed, by means of the bottling apparatus.

When the weight of the salt had been determined, the boat was placed in the weighed electrolytic cell¹ containing about 100 g. of mercury, and the salt was dissolved in water which had been used to rinse the weighing bottle. Electrolysis was then begun with a current strength somewhat less than one ampere, and was continued for about sixteen hours. During the electrolysis a slow current of very pure hydrogen was caused to bubble through the solution, in order to remove the bromine liberated at the anode. At this point the bulk of the zinc had been deposited in the mercury, and the greater part of the bromine had been expelled. The electrolyte was now removed to a clean flask by suction, and the amalgam and cell were rinsed a few times with very pure water. The electrolyte was evaporated together with a small amount of nitric and sulfuric acids in a quartz dish. The residue of zinc sulfate, together with the excess of sulfuric acid, was dissolved in water and returned to the cell, and electrolysis was continued for some hours longer. Then the cell was again washed with chilled water which had been saturated with pure hydrogen, with especial pains not to break the electrolytic circuit until all of the electrolyte had been displaced. After the water had been removed as completely as possible, the cell and the amalgam were rinsed two or three times with very pure alcohol. The cell was then stoppered and the alcohol was evaporated in a small tubular desiccator containing fused sodium hydroxide, a Geryk oil pump being used to exhaust the desiccator. The pressure at first was not reduced below a few millimeters, since the rapid evaporation of the alcohol tended to blow the stopper out of the cell, but as soon as the alcohol had disappeared, the pressure was lowered as far as possible. After standing some time in this desiccator, the cell and its counterpoise were placed in a second larger desiccator, also containing fused sodium hydroxide, and were left in a high vacuum for some hours before being weighed. In the meantime the electrolyte, together with the aqueous and alcoholic washings, was evaporated in the quartz dish previously used in the same experiment, and when the liquid had been reduced to a volume of a few cubic centimeters, it was transferred to a weighed platinum crucible, and the evaporation continued at gradually increasing temperatures until the sulfuric acid had been expelled, and nothing but the residue of zinc sulfate remained. The crucible with its contents was then weighed.

¹ Form II, Baxter and Hartmann, *THIS JOURNAL*, 37, 123 (1915).

Since in the previous work with cadmium bromide it was found that the initial weight of cadmium thus obtained is usually too large, owing probably to the formation of a small amount of mercurous bromide upon the amalgam, the electrolysis was now repeated by dissolving the zinc sulfate residue in the platinum crucible in a small amount of sulfuric acid, returning the solution to the cell, and electrolyzing for several hours. The process of washing was repeated in exactly the same way as before, the amalgam was dried and weighed, and the electrolyte was evaporated, and the residue of zinc sulfate again determined. In most cases a loss in weight of a few tenths of a milligram occurred during the first electrolysis. If this was so, the process was repeated until the total weight of zinc, as obtained from the gain in weight of the cell and the zinc sulfate residue, became constant within less than a tenth of a milligram. The results as presented in the table are computed on the basis of the final weight.

Because the process of repeated electrolysis was a laborious and time-consuming one, in several analyses the zinc bromide was converted to sulfate before electrolysis. In order to do this the boat with the fused zinc bromide was placed in a quartz dish, and the salt was dissolved in the purest water. The boat was removed with careful rinsing, the rinsings being added to the original solution. Then concentrated sulfuric acid in excess of the amount necessary to convert the bromide to sulfate was added, as well as nitric acid, and the solution was gently heated on an electric stove, in order to liberate and vaporize the bromine. The temperature, however, was kept low enough so that boiling did not actually occur. After the solution had been evaporated until the volatile matter had been expelled and the zinc sulfate had separated from the residual concentrated sulfuric acid solution, the whole was dissolved in water and evaporation repeated, in order to decompose bromide which might have been included in the solid residue during the first evaporation. The second residue was again dissolved in the minimum amount of water, and the solution was quantitatively transferred to the weighed electrolytic cell. Electrolysis was now carried out as usual. The amalgam was washed and dried, and the residue of zinc sulfate in the electrolyte was determined. This residue, while never large, was always appreciable. Although in every case the zinc sulfate residue was dissolved in sulfuric acid, returned to the cell, and electrolysis repeated, the total weight of zinc obtained was never reduced by the process. The experiments in which this modification of the procedure was employed are indicated in the table. It can be seen that the results of these experiments do not differ from those in which the bromide was electrolyzed directly.

The weights were standardized by the substitution method described by Richards. All weighings of the cell and of the weighing bottle con-

taining the zinc bromide were made by substitution for counterpoises of the same material and of the same shape and size. A vacuum correction of $+0.000140$ g. is applied for every gram of zinc bromide. This is computed from the densities 4.219 for zinc bromide¹ and 8.3 for the brass weights. A vacuum correction of $+0.000003$ g. is applied for each gram of dissolved zinc. This is computed from the density of saturated zinc amalgam at 25° as found by Crenshaw,² 13.343. This amalgam contains 2.220 g. of zinc in 100 g. of mercury.

THE ATOMIC WEIGHT OF ZINC.



$$\text{Br} = 79.916.$$

Number of analysis.	Wt. of ZnBr ₂ in vacuum. Grams.	Wt. of Zn from amalgam in vacuum. Grams.	Wt. of residue from electrolyte. Gram.	Total wt. of Zn in vacuum. Grams.	Ratio Zn : Br.	Atomic weight of zinc.
1.....	6.88781	1.99857	0.00148	1.99917	0.408942	65.362
2.....	6.79973	1.97241	0.00206	1.97324	0.408835	65.345
3.....	7.67096	2.22673	0.00096	2.22712	0.409108	65.389
4.....	8.02839	2.33109	0.00031	2.33122	0.409189	65.402
5 ^a	7.18458	2.08428	0.00219	2.08517	0.408904	65.356
6 ^a	7.55005	2.19143	0.00094	2.19181	0.409054	65.380
7 ^a	7.71332	2.23883	0.00134	2.23937	0.409096	65.387
8.....	7.11551	2.06545	0.00134	2.06599	0.409146	65.395
9.....	7.44099	2.16000	0.00115	2.16047	0.409140	65.393
10 ^a	7.18828	2.08701	0.00065	2.08727	0.409188	65.401
				Average,	0.409060	65.381
Total.....	73.57962	21.36083	0.409063	65.381
Average, omitting Analyses 1 and 2					0.409103	65.388

Since Analyses 1 and 2 were made with zinc bromide of a less degree of purity than the others, we feel that the average of Analyses 3 to 10, 65.388, represents most nearly the real outcome of the work.

Richards and Rogers,⁴ by comparing zinc bromide with silver and weighing the silver bromide formed, found the atomic weight of zinc to be 65.376 ($\text{Ag} = 107.880$; $\text{Br} = 79.916$). In other words, they found zinc bromide to contain 70.971% of bromine, while in the present research the percentage of zinc is found to be 29.033. The sum is 100.004%.

The individual results are fairly consistent among themselves, and while the agreement of the average value with that of Richards and Rogers is not absolute, it certainly affords a very satisfactory confirmation of the earlier value. Since the investigation was interrupted at this point, it seems worth while to present the preliminary results. The subject is being pursued further in this laboratory.

¹ Richards and Rogers, *Proc. Amer. Acad.*, 31, 163 (1895).

² *J. Phys. Chem.*, 14, 158 (1910).

³ Changed to sulfate before electrolysis.

⁴ *Proc. Amer. Acad.*, 31, 158 (1895).

We are greatly indebted to both the Carnegie Institution of Washington and the Elizabeth Thompson Science Fund for very generous assistance in this investigation.

CAMBRIDGE, MASS.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE.]

GADOLINIUM SODIUM SULFATE.

BY D. W. BISSELL AND C. JAMES.

Received February 10, 1916.

This investigation seemed to be of peculiar interest, since, according to some observers, gadolinium sodium sulfate was insoluble in sodium sulfate solution, while at least one other has suggested that its solubility might be used for a means of separation. Of course, the solubility of gadolinium sulfate in sodium sulfate solution might first increase and later decrease. This is true in the case of yttrium, and would explain the different observations that have been published. However, the following work shows that, when sufficient sodium sulfate was added so as to leave a slight excess, only about 0.6 g. of gadolinium sulfate was contained in a liter.

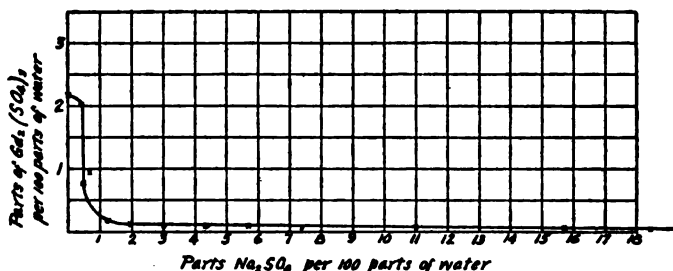
Pure hydrated gadolinium sulfate was prepared as follows: Gadolinium material was first separated from europium and less soluble earths by crystallizing the double magnesium nitrates in the presence of bismuth magnesium nitrate. The more soluble portions were then converted to the bromates and fractionated until the least soluble portions gave a pure white oxide. This bromate was converted into the oxalate and the latter treated with concentrated sulfuric acid and heated until all fumes ceased to be evolved. The anhydrous sulfate was next dissolved in water, and carefully crystallized over the steam bath. The crystals were removed, dried and finely powdered.

Bottles containing various amounts of gadolinium sulfate and sodium sulfate were made up, and about 50 cc. of water added to each. They were then rotated in a thermostat at 25° for several months. After they had settled, the liquid phase was analyzed in the following manner: Two samples were drawn from each bottle and transferred to tared weighing bottles. The first was diluted, heated to boiling, and treated with a warm solution of ammonium sebacate. The precipitate was washed free from sodium, ignited and weighed as the oxide Gd_2O_3 . The results were calculated as $Gd_2(SO_4)_3$ and as the equivalent of sulfur trioxide. The second sample was diluted, heated to boiling, acidified with hydrochloric acid and the total SO_3 precipitated as barium sulfate with barium chloride. This gave the total SO_3 , and by subtracting from this the SO_3 in combination with the gadolinium, the amount in the sodium sulfate

was obtained. The results of the analysis as parts per 100 parts of water were as follows:

Bottle.	Parts of $Gd_2(SO_4)_3$ per 100 parts of water.	Parts of Na_2SO_4 per 100 parts of water.	Bottle.	Parts of $Gd_2(SO_4)_3$ per 100 parts of water.	Parts of Na_2SO_4 per 100 parts of water.
1	2.15	0.00	10	0.06	5.71
2	2.08	0.42	11	0.05	7.46
3	2.04	0.44	12	0.05	11.02
4	0.76	0.47	13	0.06	15.74
5	0.88	0.66	14	0.05	18.54
6	0.17	1.26	15	0.05	22.02
7	0.10	1.94	16	0.05	27.05
8	0.07	3.01	17	0.05	27.40
9	0.07	4.39			

The resulting curve is shown in the figure, and is similar to that obtained for samarium sodium sulfate.¹ The solubility of the pure gadolinium sulfate at 25° was slightly lower than that given by Benedict.²



The procedure for the analysis of the solid phase was as follows: A sample was removed by means of a platinum spoon and pressed dry with filter paper. It was then well mixed and divided into two portions which were weighed. The samples were then transferred to beakers, dissolved in water acidified with hydrochloric acid, and the gadolinium and sodium sulfates determined by the methods used above. A study of the curve shows that there is probably only one compound formed between the two sulfates. The lines joining the points of the liquid and solid phases upon the triangular diagram, were so nearly parallel that the point of intersection could not be settled with accuracy. It appeared, however, that the probable ratio was one to one. In order to prove this the solid phase was taken from bottles widely separated, washed on filter paper and dried. The analyses were carried out as before described, while water was determined by difference.

	$Gd_2(SO_4)_3$.	Na_2SO_4 .	H_2O .	Ratio.
1.....	76.37	19.32	4.31	1:1:2
2.....	76.30	19.25	4.45	1:1:2

¹ THIS JOURNAL, 36, 634 (1914).

² Z. anorg. Chem., 22, 409 (1899).

This indicates that the double sulfate has the ratio 1 : 1 : 2 and the formula $\text{Gd}_2(\text{SO}_4)_3 \cdot \text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$. This is similar to the compound with potassium sulfate according to Benedict.

DURHAM, N. H.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE.]

THE EXTRACTION OF BERYLLIUM FROM GADOLINITE.

BY C. JAMES AND G. A. PERLEY.

Received February 10, 1916.

The most important elements contained in gadolinite comprise beryllium and those of the rare-earth family. Usually the first named is either neglected or else separated by the use of sodium bicarbonate or ammonium carbonate. Since the iron group precipitate contains no aluminium, or at the most mere traces, the beryllium and iron may be separated by the use of an excess of sodium hydroxide. The writers discovered a much simpler method which consists of the fractional precipitation of the hydroxides by means of sodium hydroxide. When a concentrated solution of the chlorides or sulfates of beryllium and ferric iron is precipitated with sodium hydroxide at the boiling point, ferric hydroxide, or a basic salt, is thrown down before the beryllium. If dilute solutions be used, glucinum hydroxide accompanies the ferric hydroxide and the separation is very poor. From the large number of experiments carried out, the following seems to be the simplest manner for working up the mineral:

The gadolinite was first crushed, and then finely powdered in a ball mill. Both sulfuric and hydrochloric acids were used in the attack. Although hydrochloric acid at first seems preferable, it is much inferior, since heating with concentrated sulfuric acid rapidly renders the silica insoluble. The decomposition was finally carried out in a large cast iron vessel capable of taking seventy-five kilos at a charge. The vessel was fixed in brickwork, and the mixture heated until dense white fumes of sulfuric acid were copiously evolved. The sulfated mineral was then stirred with water in a large copper tank. By adding the material slowly, the temperature was not allowed to rise, and a strong solution of the sulfates was obtained. The whole was then left until the silica had settled and the supernatant liquid had clarified. The clear liquid was siphoned off and precipitated with a hot solution of oxalic acid and allowed to stand for about twelve hours. The crystalline rare earth oxalates were filtered off and well washed with boiling water. The filtrate from the above, containing the beryllium and iron, may be treated several different ways, the best all-round method being as follows: The solution is heated and treated with some oxidizing agent, such as potassium bromate, in order to remove the oxalic acid, after which about a liter of ammonium

hydroxide is added, followed by a concentrated solution of sodium hydroxide until the odor of ammonia makes its appearance. The whole is then well boiled and the hydroxides separated by filtration. It is advisable to always test the filtrate for beryllium for fear that an excess of sodium hydroxide has been added. However, the end point as shown by the appearance of ammonia is usually very sharp. This operation may be carried out in a large copper tank fitted with a propeller. The next step consists in separating the iron and beryllium. The hydroxides are stirred with enough hydrochloric or sulfuric acid to dissolve about two-thirds of the whole. This should bring about the solution of all the beryllium together with some iron. The mass is filtered and the residue tested for beryllium. If the latter is found to be present, another extraction must be made. The acid extract is heated to boiling and carefully precipitated with sodium hydroxide until a small amount of the filtered liquid gives a light colored precipitate with ammonium hydroxide—showing that nearly all the iron has been removed. The liquid is separated by filtration, again heated to boiling, treated with a small amount of sodium hypobromite and precipitated with sodium hydroxide until a small amount of the liquid gives a white precipitate of hydroxide when treated with ammonium hydroxide. The mass is filtered and the filtrate separated from the last traces of iron by adding sodium hydrogen sulfide. The two last residues which contain beryllium are worked up with the next lot. The addition of ammonium acetate and hydrogen sulfide before the sodium hydrogen sulfide helps in the separation of traces of copper and iron, but causes trouble in the final precipitation of the basic beryllium carbonate. The addition of too much hypobromite prevents the rapid separation of the last traces of iron, owing to oxidation of the sulfide produced. After the removal of all the iron, the beryllium is thrown down as the basic carbonate by adding a concentrated solution of sodium carbonate to the boiling liquid. After thoroughly boiling, the precipitated basic carbonate is filtered off and well washed with boiling water. It is necessary to test all the final filtrates, and to boil off all hydrogen sulfide before precipitating the beryllium as basic carbonate, otherwise a product giving a greenish oxide is obtained.

Another method for preparing beryllium basic carbonate from the filtrate after the separation of the rare-earth oxalates is applicable only when the liquid is very rich in beryllium. The liquid containing the iron and beryllium is oxidized to remove the oxalic acid and to convert the iron to the ferric condition, and then precipitated while boiling with sodium hydroxide until nearly all the iron is removed. The last portions of iron are removed by more sodium hydroxide and sodium hydrogen sulfide as described above.

These methods for the separation of iron and beryllium, although of

no use quantitatively, are by far the best on the large scale, since the various stages can be carried out with great rapidity. The resulting beryllium product is entirely soluble in sodium bicarbonate, a test which Parsons has shown to be very delicate. The separation of aluminium from beryllium will be described in a later paper.

DURHAM, N. H.

[CONTRIBUTION FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

A STUDY OF INDICATORS FOR THE DETERMINATION OF TEMPORARY HARDNESS IN WATER.

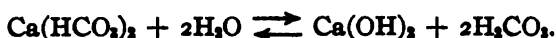
BY JOHN F. NORTON AND H. L. KNOWLES.

Received February 4, 1916.

Temporary hardness in water is due largely to the presence of calcium and magnesium bicarbonates. On heating, these decompose according to the equation



The bicarbonates, being salts of a weak acid and a relatively strong base, are hydrolyzed in solution, imparting alkaline properties to the water.



The most rapid and satisfactory method for determining temporary hardness is by titration of the alkali with standard acid in the presence of a suitable indicator. For this latter purpose, methyl orange is in quite general use, although the committee on Standard Methods¹ of Water Analysis recommends lacmoid, crythrosine or phenacetolin.² Peters³ suggests alizarine, while Blacker⁴ claims that dimethylamidoazobenzene gives good results. Howard⁵ and Pope recommend methyl red and certain of its derivatives. Reichard⁶ offers an inorganic indicator—bismuth oxyiodide.

Indicators are weak tautomeric acids or bases. According to Noyes⁷ the fundamental equations upon which the theory of indicators is based are:

$$(\text{H}^+) = \frac{1-\alpha}{\alpha} \frac{K_{IA}}{\gamma}$$

for acid indicators and

¹ "Standard Methods of Water Analysis," *Am. Pub. Health Assn.*, 1912, p. 37.

² We are informed that the next report on Standard Methods will give preference to methyl orange.

³ *Apoth. Ztg.*, 18, 25 (1903).

⁴ *Chem. Ztg.*, 37, 56 (1912).

⁵ *J. Chem. Soc.*, 99, 1333 (1911).

⁶ *Pharm. Zentr.*, 53, 1033 (1912).

⁷ THIS JOURNAL, 32, 815 (1910).

$$(\text{OH}^-) = \frac{\alpha}{1-\alpha} \frac{K_{\text{IB}}}{\gamma}$$

or

$$(\text{H}^+) = \frac{1-\alpha}{\alpha} \frac{K_w \gamma}{K_{\text{IB}}}$$

where α = fraction of indicator transformed; γ = ionization of indicator salt formed; K_{IA} and K_{IB} = ionization constants of acid and basic indicators, respectively; H^+ and OH^- = concentration of these ions in mols per liter; K_w = ionization constant of water. "These equations express the principle that in any titration with a given indicator the end point (determined by color change) is reached when the H^+ concentration in the titrated solution attains a definite value. This value varies with the ionization constant of the indicator and the fraction transformed."¹

It can be shown mathematically that α should always be a relatively small value, usually not greater than 25% if accurate results are to be obtained.

The use of indicators in water analysis differs from their use in ordinary volumetric work on account of the presence of a variety of salts, and of weak acids, both organic and inorganic, which may have a very decided effect on the results obtained.

Walker and Kay² have suggested that the alkalinity or acidity of a water be expressed in terms of the hydroxyl or hydrogen-ion concentration. It will be seen at once that this will have little relation to the temporary hardness, which should also include the "reserve"³ alkalinity or acidity.

The problem before us is to determine the range of hydrogen-ion concentrations corresponding to a complete neutralization of the bicarbonates by an acid, including the effect of the presence of other salts and of carbonic acid. Knowing this, we will then choose a series of indicators having the proper constants. This series will then be subjected to a practical test on waters of known composition, after first ascertaining the best end point for each indicator.

Since sulfate of alum is in common use for the purification of water supplies, it seems desirable to have an indicator which will be sensitive to the acidity produced by this salt. Comparative tests will therefore be made to determine this property.

Experimental Part.

Hydrogen-Ion Concentration in Titrated Waters.—To determine this a series of four waters was conceived, analogous in composition to neutral waters so far as concerns those constituents which might affect indi-

¹ THIS JOURNAL, 32, 821 (1910).

² J. Soc. Chem. Ind., 31, 1013 (1912).

³ Washburn, Proc. Ill. Water Supply Assn., 93, 101 (1910).

cator end points (Table I). Solutions were then made up to represent the composition of these waters after the bicarbonates had been neutralized with hydrochloric acid (Table II).

TABLE I.
Composition of Synthetic Waters.

	Parts per million.			
	I.	II.	III.	IV.
Ca(HCO ₃) ₂	61	122	202	243
Mg(HCO ₃) ₂	30	60	60	90
MgSO ₄	25	25
CaCl ₂	28	28
H ₂ CO ₃	20	40	80	100

TABLE II.
Composition of Synthetic Waters.
"After Titration."

	Parts per million.			
	I.	II.	III.	IV.
CaCl ₂	42	83	140	194
MgCl ₂	20	39	39	59
MgSO ₄	25	25
H ₂ CO ₃ ¹	92	184	287	409

The hydrogen-ion concentration of each of these waters was then determined by the method suggested by Walker and Kay,³ and the following results obtained:

Water.	I.	II.	III.	IV.
H ⁺ conc.	5×10^{-8}	10^{-8}	2×10^{-8}	3×10^{-8}

On the basis of these results it was decided to test only those indicators which change color between H⁺ ion concentrations of 10^{-4} and 10^{-8} . The three recommended by Standard Methods were also included. Table III gives a list of those chosen, together with the H⁺ ion concentration at the color change, and the composition of the indicator solutions.

TABLE III.—INDICATORS.

Indicator.	H ⁺ conc. at color change. ²	Soln. g. per 100 cc.
Dimethylamidoazobenzene (butter-yellow)	10^{-4}	0.2 95% alcohol
Sodium alizarine sulfonate.....	10^{-6}	0.1 water
Methyl red.....	10^{-6}	0.1 95% alcohol
Gallein.....	10^{-6}	0.1 water
Methyl orange.....	10^{-8}	0.1 10% alcohol
Lacmoid.....	0.1 95% alcohol
Erythrosine.....	0.01 water
Phenacetolin.....	0.2 50% alcohol

An inorganic indicator, bismuth oxyiodide, was also made up according to directions given by its discoverer, Reichard.⁴ A light yellow solution resulted, of color intensity equal to that given by a few drops of methyl orange in 100 cc. of water. In the presence of alkali this indicator became colorless, but a subsequent addition of acid failed to reproduce but a part of the original yellow. Because of this fact, and of its small coloring power, this indicator appeared to be impracticable.

¹ It has been assumed that H₂CO₃ has not escaped in titrating.

² *J. Soc. Chem. Ind.*, 31, 1013 (1912).

³ *Salm., Z. physik. Chem.*, 57, 471 (1906).

⁴ *Pharm. Zentralblat*, 33, 1033 (1912).

Determination of Color for End Point.—The determination of a practical working end point for each indicator was next considered. To accomplish this, 1 to 2 cc. of the indicator (according to its color strength), were added to 100 cc. of water. To half of this were added 1 to 2 cc. of strong acid and to the other 1 to 2 cc. of strong alkali. This gave the two color forms of the indicator corresponding to 100% transformation. Thus in the case of butter-yellow or methyl orange, a yellow- and a red-colored solution were obtained. The solution containing the alkali was then poured into a "Petri" dish. Portions of the acid colored solution, say 5 cc., $7\frac{1}{2}$ cc., and 10 cc., were taken and diluted to 50 cc. with distilled water. The solutions thus obtained were poured into "Petri" dishes. By placing these dishes successively over that containing the alkali-colored solution, the color at end points corresponding in this case to 10%, 15% and 20% change from alkaline to acid reaction of the indicator was approximately obtained. To get the true color at the end point, which by trial in this way proved to be a good one, a portion of the alkali-colored solution equal to that of the acid-colored solution used to give this suitable end point color, was taken out and replaced by distilled water. Thus if a good end point for butter-yellow was given by a 15% transformation, $7\frac{1}{2}$ cc. of the yellow alkali solution would be replaced by water, giving, when the two colors were combined (85% yellow and 15% red), the true color at an end point corresponding to 15% transformation of the indicator.

By such a knowledge of the fraction of the indicator transformed from the color in alkaline solution to that in acid solution, an end point to which that indicator could always be titrated was definitely fixed; and the need, therefore, of endeavoring to remember the color at this suitable end point was eliminated. The indicators studied in this way, and their fractions transformed from alkaline solution to acid at a suitable end point are given in Table IV.

TABLE IV.

Indicator.	Fraction transformed. Per cent.	Indicator.	Fraction transformed. Per cent.
Butter-yellow ¹	12	Lacmoid.....	25
Sodium alizarine sulfonate.	30	Phenacetolin.....	25
Methyl red.....	10	Methyl orange.....	15
Gallein.....(about)	100		

Gallein was discarded because of its very indefinite end point.

Titration with Indicators.—With the indicators thus chosen and their suitable end points known, a series of waters was made up and titrated. In titrating, 100 cc. Nessler tubes were used in place of the "Petri" dishes, the shade given by these two tubes when held one before the other, and

¹ Dimethylamidoazobenzene: For convenience this will be hereafter designated by its trade name, Butter-yellow.

viewed by transmitted light, gave the color at the determined satisfactory end point. Table V gives the composition of the artificial waters used, while Table VI shows the results obtained in titrating 100 cc. of the water with hydrochloric acid (about 0.008 N).

TABLE V.
Composition of Artificial Waters, Series No. 1.

	Parts per million.			
	I.	II.	III.	IV.
$\text{Ca}(\text{HCO}_3)_2$	14.8	29.6	49.2	59.1
$\text{Mg}(\text{HCO}_3)_2$	30.0	60.0	60.0	90.0
MgSO_4	25.0	25.0
CaCl_2	28.0
H_2CO_3	9.0	22.0	22.0	28.0

TABLE VI.
Titration of Artificial Waters, Series No. 1.

	I.	II.	III.	IV.
Hardness (calculated) ¹	29.6	59.4	71.4	98.0
Indicator.	Hardness found.			
Methyl red (1 mg.).....	12.8	30.2	36.1	48.6
Sodium alizarine sulfonate (2 mg.)..	5.7	7.8	7.4	8.6
Methyl orange (1 mg.).....	25.9	54.0	64.5	87.4
Lacmoid ² (2 mg.).....	24.8	52.3	63.0	85.5
Phenacetolin ³ (4 mg.).....	23.6	52.4	63.1	86.5
Butter-yellow (0.5 mg.).....	29.6	59.6	71.5	98.6

These results show clearly that butter-yellow is the best indicator to use in titrating bicarbonates in the presence of carbonic acid. Methyl orange, methyl red and sodium alizarine sulfonate give low results, while lacmoid and phenacetolin not only give low figures, but it was found that a series of end points could be obtained by varying the heating of the solution before final titration. To determine the end point to which methyl orange would have to be titrated in order to give accurate results in the case of water No. IV, 100 cc. were taken, 1 mg. of indicator added and the required amount of acid for neutralization run in. The color of this solution was a deep orange and corresponded to over 50% transformation of the indicator. Such an end point is hardly practicable.

Butter-yellow was next compared with erythrosine. The latter was used both in the presence of ether and of chloroform, the titration in both cases being done in glass-stoppered bottles. The ether solution was made by dissolving 0.025 g. of indicator in 100 cc. of ether which had been washed with weak alkali and then with distilled water until it was neutral to rosolic acid. 10 cc. of this ether solution were added to the water to be titrated. Using erythrosine in conjunction with chloroform,

¹ Approximate.

² Hardness expressed as parts of CaCO_3 per million.

³ Solution brought to boiling before finishing titration.

2.5 cc. of a water solution of indicator (1 : 10000) and 5 cc. of neutral chloroform were added. As this amount of indicator was found to give low results, the amount was increased to 5 cc. Table VII gives the composition of the waters used and Table VIII the results obtained.

TABLE VII.
Composition of Waters I to III, Series No. 2.

Salt.	Parts per million.		
	I.	II.	III.
Ca(HCO ₃) ₂	30.0	70.0	100.0
Mg(HCO ₃) ₂	10.0	30.0	40.0
CaCl ₂	10.0	20.0	30.0
MgSO ₄	5.0	10.0	20.0
H ₂ CO ₃ ¹	1.0	2.0	2.0

TABLE VIII.
Titration of Waters I to III, Series No. 2.

	I.	II.	III.
Hardness (calculated).....	25.4	63.8	89.2
Indicator.	Hardness found.		
Butter-yellow (1/4 mg.).....	26.3	64.5	88.8
Erythrosine (in ether).....	26.0	62.7	83.1
Erythrosine ² (2.5 cc.).....	24.7	61.1	82.9
Erythrosine ² (5 cc.).....	25.6	63.0	83.6

Erythrosine also gives slightly lower results than butter-yellow, the discrepancy increasing with the hardness. Ether solution is slightly better than chloroform, but not sufficiently so to overcome the disadvantage of the ether due to the escape of small amounts when the stopper is removed from the bottle. Butter-yellow has again been shown to give excellent results.

In order to still more rigidly test the effect of the presence of carbonic acid, waters containing excessive amounts were analyzed with the results as shown in Table IX.

TABLE IX.
Analysis of Waters I and II, Series No. 3.

	Parts per million.		
	I.	II.	III.
Hardness (calculated).....	22.0	66.9	95.9
H ₂ CO ₃	1110.0	1150.0	117.0
	Hardness found.		
Lacmoid (100 % trans.).....	22.4	64.3	90.9
Erythrosine (5 cc.).....	16.8	51.6	80.0
Butter-yellow (1/4 mg.).....	22.6	63.1	95.6

Sensitiveness of Indicators to Alum.—It is sometimes necessary to use an indicator which is sensitive to small amounts of acid such as exist in waters which have been overdosed with alum. The indicators used

¹ Approximate.

² In chloroform.

above were therefore tested to determine their sensitiveness to alum by adding a known alum solution to 100 cc. of distilled water containing the indicator, until the color change was obtained. The color was then duplicated by using standard acid. The results are given in Table X.

TABLE X.
Sensitiveness of Indicators to $\text{Al}_2(\text{SO}_4)_3$.

Indicator.	$\text{Al}_2(\text{SO}_4)_3$ added (in parts per million).	Cc. HCl corresponding.
Butter-yellow.....	25	0.3
Methyl orange.....	15	0.3
Phenacetolin ¹	3	0.1
Lacmoid ¹	2	0.1
Butter-yellow ¹	10	0.3

Sodium alizarine sulfonate, erythrosine and congo red were tried, but found impracticable on account of color lake formation. When phenacetolin and lacmoid were used, the solution was previously heated in order to have conditions the same as in the determination of alkalinity with these indicators. It is evident from the above values that lacmoid and phenacetolin are the most sensitive indicators, while butter-yellow is in about the same class with methyl orange.

Since lacmoid possessed the admirable quality of being highly sensitive to alum, an effort was made to increase the accuracy of this indicator in the determination of alkalinity. The end point of the indicator was, therefore, extended from a 25% transformation to nearly 100%, or total transformation; that is, to a red. This end point, it may be observed, is one which approaches more closely that obtained by using lacmoid according to the procedure given by Standard Methods for the determination of alkalinity. Table IX gives the data and it is evident that but little better results were obtained.

Accurate End Point for Butter-Yellow.—In order to always titrate to the same end point, and still avoid the rather long method for obtaining it as described above, the following directions were worked out, which give the proper color with a minimum of effort. To 100 cc. of distilled water add 0.1 cc. of an alcoholic solution of butter-yellow (2 : 1000) and 0.40 cc. of 0.02 *N* sulfuric acid. Titrate the unknown solution, containing the same amount of indicator, until the color matches that of the standard.

Summary.

(1) Butter yellow (dimethylamidoazobenzene) is the best indicator to use in titrating the bicarbonate alkalinity (temporary hardness) of natural waters.

(2) Lacmoid gives the best results in the presence of alum, but low results are obtained in determining bicarbonates. For low alkalinities

¹ Temperature of solution 90–95°.

the difference is negligible, but its use is not to be recommended where the alkalinity is over 100.

(3) A standard color is recommended for titrations with butter-yellow.

BOSTON, MASS.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF VIRGINIA.]

A RAPID METHOD FOR THE ESTIMATION OF COPPER AND IRON.

By GRAHAM EDGAR.

Received January 27, 1916.

The insolubility of cuprous thiocyanate in dilute acid solutions has formed the basis for a number of methods for the estimation of copper. Without attempting to give complete references to the literature on this subject it may be pointed out that Rivot¹ and Van Name² have shown that the gravimetric estimation of copper as cuprous thiocyanate is accurate under properly regulated conditions, while Volhard,³ Guess,⁴ Jamieson,⁵ and others, have based volumetric processes upon the same precipitation. The accuracy of the volumetric processes seems to be questioned by many reference books on analytical chemistry. Thus Low⁶ states that cuprous thiocyanate is sufficiently soluble to necessitate the use of empirical tables in calculating the results of Guess's method, while Sutton⁷ states that Volhard's method is inapplicable in the presence of iron. These statements seem to be contradicted by the results obtained by Van Name, Volhard, and by the results given in the present paper.

While engaged in the investigation of certain reactions of cuprous thiocyanate the writer was impressed by the simplicity and accuracy of the Volhard method, and carried out preliminary experiments which resulted in a modification of the Volhard procedure by which not only copper, but iron associated with it, may be rapidly and accurately estimated. The principles involved are as follows: (1) the copper is precipitated as cuprous thiocyanate and iron reduced to the ferrous state by the action of sulfur dioxide and standard NH_4CNS solution; (2) the excess of sulfur dioxide is removed by boiling, a current of carbon dioxide being passed into the solution meanwhile. The solution is then cooled and filtered; (3) the filtrate is treated with an excess of standard AgNO_3 solution, and is then titrated for iron with standard KMnO_4 solution; (4) the

¹ *Compt. rend.*, 38, 868 (1889).

² *Z. anorg. Chem.*, 26, 230 (1901).

³ *Z. anal. Chem.*, 18, 285 (1879).

⁴ Low, "Techn. Meth. of Ore Analysis," 7th ed.

⁵ *THIS JOURNAL*, 30, 760 (1909).

⁶ *Loc. cit.*

⁷ "Vol. Meth. of Anal.," 10th ed., p. 200.

copper is then determined by titrating the silver present in excess in the solution with standard NH_4CNS .

The technique finally adopted is as follows: The solution containing copper and iron, together with some sulfuric acid, is nearly neutralized with NH_4OH or Na_2CO_3 . It is then saturated with sulfur dioxide (either by passing the gas into the solution, or by adding a solution of the gas in water, or a solution of ammonium bisulfite) and heated to incipient boiling. At this point sufficient standard NH_4CNS solution is added from pipet or buret to precipitate all of the copper. With a little practice there is no difficulty in determining when an excess has been added. The iron is usually not completely reduced at this time, and the reddish color of ferric thiocyanate persisting for a few moments throughout the solution serves to show that the precipitation of copper is complete; or the precipitate may be allowed to settle a little, and the supernatant liquid tested with additional NH_4CNS . The solution is then boiled vigorously for ten minutes, a current of carbon dioxide being meanwhile passed into it. This serves to remove the last traces of sulfur dioxide, and the boiling serves to coagulate the precipitate and render it easily filtrable. After the boiling the flask containing the solution is placed in cold water to cool for a few minutes, the current of carbon dioxide being kept up in order to prevent the re-oxidation of the hot ferrous solution. The solution is now filtered through paper, or preferably through asbestos, and is washed with cold water. It shows no tendency whatever to run through the filter. The filtrate is treated with a few cc. of dilute sulfuric acid, and then there is added sufficient standard AgNO_3 solution to precipitate the excess of NH_4CNS . (If desired a little ferric sulfate may be added to show when precipitation is complete.) The solution is now titrated for iron with standard KMnO_4 solution in the usual way. When the end point is reached the color of the KMnO_4 is removed by the addition of a trace of ferrous sulfate, and the excess of silver present in the solution is at once determined by titration with standard NH_4CNS solution. If there is much iron present it will serve as indicator, otherwise ferric sulfate solution may be added for this purpose.

The iron is calculated in the usual way from the amount of KMnO_4 solution used; the copper is calculated from the difference between the total volume of ammonium thiocyanate and the volume equivalent of the silver nitrate (solution) added (1 cc. of 0.1 N NH_4CNS is equivalent to 0.006357 g. of Cu).

The whole determination requires practically no more time than that usually required for the estimation of copper alone, and in addition is highly accurate, as the results in Table I show.

The method is admirably adapted to the analysis of ores. In most cases the ore is decomposed with conc. HNO_3 and conc. HCl in the usual

way. It is then heated with H_2SO_4 until all of the HNO_3 and HCl , and most of the H_2SO_4 has been removed. After diluting with water it is in most cases ready for treatment as described above, without even filtering off the insoluble residue. Of course in the case of ores not decomposable by the acid treatment, fusion methods may be adopted, the technique being thereafter modified accordingly. Silver, if present in sufficient quantity, must be removed as chloride by filtration, before evaporating with H_2SO_4 .

TABLE I.

Standard solutions of copper sulfate and ferric alum were mixed in varying proportions, diluted to about 50 cc., and analyzed as described above.

No.	Cu taken. G.	Cu found. G.	Error Cu. G.	Fe taken. G.	Fe found. G.	Error Fe. G.	NH_4CNS^1 for ttr. cc. $N/10 \times 1.3156$.	KMnO_4 cc. $N/10 \times 1.0024$.
1	0.0318	0.0318	± 0.0000	1.40	... ²
2	0.0318	0.0317	-0.0001	1.38	... ²
3	0.0636	0.0635	-0.0001	5.19	... ²
4	0.0636	0.0634	-0.0002	0.2464	0.2464	± 0.0000	5.17	44.00 ³
5	0.0636	0.0635	-0.0001	0.1232	0.1233	$+0.0001$	5.19	22.02 ³
6	0.0318	0.0319	$+0.0001$	0.2464	0.2466	$+0.0002$	1.41	44.04 ³
7	0.0636	0.0635	-0.0001	0.0493	0.0493	± 0.0000	5.18	8.80 ³
8	0.1589	0.1589	± 0.0000	0.0246	0.0246	± 0.0000	1.60	4.40 ³
9	0.0636	0.0635	-0.0001	0.1232	0.1231	-0.0001	5.19	21.98 ³
10	0.0636	0.0636	± 0.0000	0.1232	0.1232	± 0.0000	5.21	22.00 ³
11	0.0318	0.0318	± 0.0000	0.1232	0.1234	$+0.0002$	1.39	22.04 ³
12	0.0636	0.0635	-0.0001	0.1232	0.1232	± 0.0000	5.19	22.00 ³

In the writer's experience the method is much more rapid than the iodide process of Low⁴ for copper, and gives the amount of iron present without an additional determination.

As an example of the applicability of the method to the rapid analysis of ores the following will serve:

An ore analyzed for copper by Low's method gave 13.05 and 13.07% Cu in two determinations. The same ore analyzed by the method proposed above gave 13.12 and 13.12% Cu, and 45.44 and 45.50% Fe in two determinations. The time required for determining both copper and iron by the new procedure was considerably less than that required for the determination of copper alone by the Low method.

Summary.

A modification of Volhard's method for the estimation of copper is suggested by which copper and iron may both be determined in the same

¹ In Expt. 8, 25 cc. of NH_4CNS were used for precipitation of the CuCNS . In all of the others 10 cc. were used. In every experiment the excess of NH_4CNS was precipitated by the addition of 10 cc. of 0.1 N AgNO_3 . The figures in Col. 7 refer to the final titration.

² Reduced with SO_2 .

³ Reduced with NH_4HSO_3 .

⁴ *Loc. cit.*

solution, the copper being precipitated as cuprous thiocyanate by standard NH_4CNS solution and the iron estimated by titration with standard KMnO_4 solution.

This method gives highly accurate results for both elements and requires a minimum of time for its completion.

The method is especially adapted to the rapid estimation of copper and iron in ores.

UNIVERSITY OF VIRGINIA.

NOTES.

Note on the Blackening of Yellow Phosphorus.—The sticks of yellow phosphorus in two laboratories in Colombo were found in time to become covered with a dull black coating. In one case the phosphorus had been kept in a stone jar and in the other in a glass bottle in a dark store-room. The experiments recorded below were undertaken with the object of discovering the nature and cause of the blackening.

A quantity of yellow phosphorus was purified by melting under a solution of potassium bichromate and concentrated sulfuric acid and leaving overnight; the still liquid phosphorus was then washed many times with distilled water and was solidified in the form of small globules by violent shaking.

Small quantities of the pure phosphorus were sealed up in glass tubes, two of which (A) contained distilled water and two (B) tap water (any oxygen in the small air space would soon be absorbed by the phosphorus). Small quantities were also placed in glass bottles loosely plugged with cotton wool to exclude dust and two of these bottles (C) contained tap water and two (D) distilled water.

One of each of the vessels A, B, C and D was placed in a dark cupboard and the remaining four were kept in the light. The contents were examined after seven months. The sealed tubes containing distilled and tap water which were kept in the dark, appeared to have undergone no change, while the corresponding tubes which had been kept in the light merely showed reddening due to the formation of red phosphorus. Another tube which contained melted phosphorus and distilled water and which had been kept in the light also, became covered on the surface with red phosphorus but still remained liquid at the end of seven months and only solidified on shaking vigorously; an interesting example of supercooling.

In the case of the vessel whose contents were exposed to air both those containing tap water showed slight blackening, while that containing distilled water and kept in the dark had a white coating, the nature of which is still being investigated; possibly the white coat is the suboxide P_4O , the existence of which has been asserted by Michaelis and Pitsch¹ and

¹ *Ber.*, 32, 337 (1899).

others but was denied by Chapman and Lidbury¹ and by Burgess and Chapman.²

The experiments seemed to indicate that the blackening is caused by some impurity in the tap water, the negative results in the case of the sealed tubes containing tap water being due to the much smaller quantity of water used than in the case of the bottles.

A small quantity, 2 or 3 g., of the black coating was obtained by scraping the sticks under water; the black solid was shaken with carbon disulfide, separated and heated in a crucible; by this means all traces of phosphorus must have been removed; the solid was then heated with concentrated nitric acid to dryness several times and the residue was extracted with dilute sulfuric acid and was tested for the metals with a positive result for copper; the remaining solid was again treated with nitric acid and this solution gave the test for phosphoric acid with ammonium molybdate.

Vogel, in 1836,³ stated that yellow phosphorus acts on copper sulfate solution with the production of copper phosphide. The reaction has been studied by Straub,⁴ who found that a dark film of copper phosphide was formed on yellow phosphorus in two months with a solution containing only one gram molecule of copper sulfate in one million liters of water.

A piece of copper wire was cleaned and placed in distilled water with some pure phosphorus and in two days both the wire and the phosphorus were covered with black phosphide. It seems likely, therefore, that the blackening observed was due to small traces of copper salts derived either from the water taps or from the copper tongs used to remove the phosphorus from the water (in another laboratory here, where only iron tongs are used, no blackening was observed). The experiments make it clear that phosphorus should be kept in distilled water, in stoppered jars, in the dark, and that iron tongs should be used to remove the sticks when necessary.

WILLIAM NORMAN RAE.

CLEVELAND MEDICAL COLLEGE,
February 14, 1916.

Saponification of Esters.—We are repeating the work on the saponification of esters by aqueous solutions of salts, and find values for methyl acetate which are lower than those earlier recorded in *THIS JOURNAL*, 38, 105 (1916). This is especially true of some of the strongly hydrated salts.

Furthermore, the results that we are now obtaining under apparently the same conditions are not satisfactorily concordant with one another.

¹ *J. Chem. Soc.*, 75, 973 (1899).

² *Ibid.*, 79, 1235 (1901).

³ *J. prakt. Chem.*, 8, 109 (1836).

⁴ *Z. anorg. Chem.*, 35, 460 (1903).

We are unable to explain fully the lower values now being found and the lack of concordance of the results. The latter fact would indicate the presence of some unknown catalyzer, possibly the surface of the glass vessels in which the reaction takes place.

The work is being pushed forward as rapidly as possible, and we hope in the near future to throw more light on this phase of the problem.

H. C. JONES.

BALTIMORE, MD.

CORRECTIONS.

"The Calomel Standard Cell," by G. F. Lipscomb and G. A. Hulett, THIS JOURNAL, 38, 20.

Page 24. Column "July 12," 0.67098 should be 0.67078.

Column "Apr. 24," 0.67044 should be 0.67024.

Page 25, line 9. .0525(T — 25)² should be —.0000025(T — 25)².

Page 25, line 15. For 0.67159 read 0.67139.

Page 25, line 18. For 0.67159 read 0.67139 and for 30060 read 30047.

Page 25, line 22. For HgCl₂ read Hg₂Cl₂.

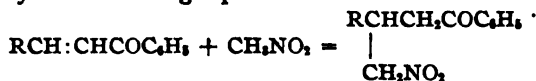
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

THE ADDITION OF ALIPHATIC NITRO COMPOUNDS TO UNSATURATED COMPOUNDS.

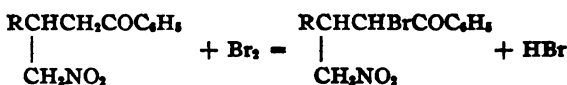
By E. P. KOHLER.

Received January 20, 1916.

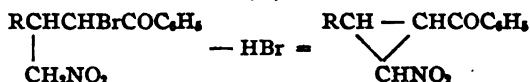
The object of this investigation was to find a method for preparing cyclopropane derivatives that have a nitro group in combination with one of the carbon atoms of the ring. Substances of this type are unknown and they cannot be made by any of the means commonly employed for making aliphatic nitro compounds. It was necessary, therefore, to make a suitable aliphatic nitro compound first and then to close the cyclopropane ring. A promising series of reactions for this purpose is represented by the following equations:



(I).



(II).



(III).

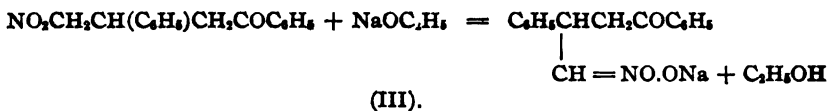
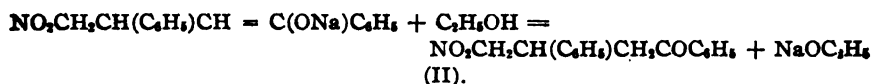
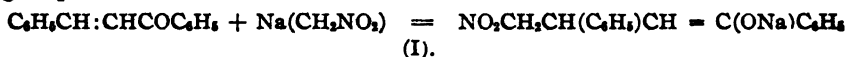
their entire behavior shows that they are constituted like the metallic derivatives of the nitroparaffins. Thus the sodium compound obtained by adding sodium nitromethane to benzalacetophenone, does not react with alkyl halides but readily reacts with bromine, giving sodium bromide and two isomeric monobromo derivatives of the nitroketone. These isomeric bromine compounds are soluble in sodium methylate, and the solutions rapidly decolorize one equivalent of bromine. Both solutions yield the same dibromo derivative, $C_{16}H_{13}O_3NBr_2$. This behavior is typical of the metallic derivatives of nitroparaffins. There is also direct evidence as to the structure of these bromine compounds. Halogen nitro compounds in which the halogen is in combination with the carbon that holds the nitro group are easily reduced. When bromonitroethane, for example, is boiled with alcoholic potassium iodide, iodine is liberated and the bromine compound is rapidly reduced to nitroethane. All the bromine compounds described above give the same reaction, and give it with the same ease, the dibromo compound passing into one of the monobromo derivatives and the two monobromo derivatives being reduced to the nitroketone.

The sodium compound obtained by adding sodium nitroethane to benzalacetophenone also readily reacts with bromine, but the resulting monobromo derivative is no longer soluble in sodium methylate, showing the absence of hydrogen on the carbon atom that holds the nitro group. The structure of the sodium and bromine compounds is therefore represented by the formulas



The result obtained with benzalacetophenone and sodium β -nitropropane supports these conclusions. The reaction in this case does not give a metallic derivative but gives, instead, the nitroketone and sodium alcoholate.

These facts show that the product obtained from the reaction between benzalacetophenone and sodium nitromethane is the result of the following steps:



When bromine is allowed to react with the nitroketones themselves it forms another pair of bromine substitution products quite different from those obtained from the sodium derivative. Alcoholic potassium iodide transforms these, quantitatively, into the corresponding iodine compound, and sodium alcoholate rapidly removes hydrobromic acid to form a cyclopropane derivative. These bromine compounds therefore have bromine in the α -position to carbonyl, and the problem of getting nitrocyclopropane derivatives is solved.

Although this paper deals only with the addition of nitroparaffins to benzalacetophenone, work now in progress shows that, under proper conditions, aliphatic nitro compounds combine quite generally with α,β -unsaturated ketones, with many unsaturated esters, unsaturated nitriles, and even with unsaturated nitro compounds. The products obtained by these reactions are far more tractable substances than the nitroparaffins with simpler alkyl groups, and we expect them to be useful not only in connection with the chemistry of cyclopropane but also with that of nitro compounds.

EXPERIMENTAL PART.

I. Benzalacetophenone and Nitromethane.

Nitromethane itself apparently does not combine with benzalacetophenone. A solution of the ketone in the nitro compound can be boiled for days without any effect beyond a very slow decomposition of the nitro compound. The result is the same when a solution of the two substances in a perfectly dry, indifferent solvent, like ligroin or benzene is heated. In boiling alcohols and in the presence of water the nitro compound disappears, but the ketone remains unchanged. By adding a small quantity of diethylamine or piperidine the addition can be carried out in any suitable solvent. In the case of methyl ketones like benzalacetone and mesityl oxide this is the best procedure, but with benzalacetophenone a better yield and a purer product can be obtained by using sodium alcoholate as condensing agent.

A small quantity of sodium alcoholate is sufficient to cause rapid disappearance of both ketone and nitro compound; but under these conditions the result is always a mixture of complex products. These are due to the fact that the sodium compound formed from one molecule each of ketone and sodium nitromethane readily combines with more of the unsaturated ketone. In order to prevent the formation of complex products, therefore, it is necessary to have an excess of sodium nitromethane *in solution*. The following procedure gives satisfactory results: A solution of 15 g. of sodium in 120 g. of dry methyl alcohol is added, with constant shaking, to a solution of 104 g. of benzalacetophenone and 37.5 g. of nitromethane in 175 g. of the same solvent. The solutions should

be at about 40° at the outset in order to prevent separation of solid sodium nitromethane, and the alcoholate should be added as rapidly as is possible without separation of solid sodium compound. The reaction is complete a few minutes after the last alcoholate has been added. The yellow liquid is then cooled and immediately acidified with glacial acetic acid. A part of the nitroketone usually begins to separate as an oil, but this soon solidifies and the remainder is slowly deposited in clear, white needles. The flask containing the product is finally cooled in a freezing mixture, the solid filtered off, thoroughly washed with weak alcohol and water, and purified by recrystallization from alcohol. A small additional amount of the product can be obtained by combining aqueous and methyl alcoholic filtrates but the resulting precipitate is far less pure and should be recrystallized separately. The best yield obtained was 92% of pure product, the average yield in a number of preparations 88.5%.

Calc. for $C_{16}H_{18}O_3N$: C, 71.4%; H, 5.4%. Found: C, 71.3%; H, 5.7%.

γ -Nitro- β -phenylbutyrophenone, $NO_2CH_2CH(C_6H_5)CH_2COC_6H_5$, crystallizes in thin, white needles that melt at 103° . It is readily soluble in benzene, acetone, chloroform, and hot alcohols; sparingly in cold alcohol and ether; insoluble in petroleum ether. A solution in acetone does not reduce permanganate, indicating the absence of unsaturation. When treated with semicarbazide in the usual way, it gives a sparingly soluble semicarbazone, proving the presence of carbonyl. The semicarbazone crystallizes in small plates and melts at 165° .

Calc. for $C_{17}H_{18}O_3N_4$: N, 17.1%. Found: N, 17.5%.

Sodium Aci-nitrophenylbutyrophenone.—The nitroketone dissolves very sparingly in concentrated aqueous alkalis, somewhat better in alcoholic potassium hydroxide, very readily in solutions of alcoholates. The pure solid sodium derivative was obtained by three different methods, all of which ultimately gave the same substance. When a mixture of dry ether and ligroin is added to the concentrated methyl alcoholic solution obtained by adding sodium methylate to nitromethane and benzalacetophenone, it generally produces a pale yellow crystalline precipitate. This was filtered off in a current of dry air, washed with absolute ether and analyzed. Analyses from different preparations gave variable amounts of sodium, but all of them lost weight (methyl alcohol) when kept over sulfuric acid in a vacuum desiccator. The final results were as follows:

Calc. for $C_{16}H_{14}O_3NNa$: Na, 7.9%. Found: Na, 7.6%

All these preparations were tinged with yellow.

A better method for getting the sodium compound is to saturate a cold solution of sodium methylate in methyl alcohol with pure nitroketone, filter from excess of ketone, and allow the filtrate to evaporate in a vacuum desiccator containing sulfuric acid. Here too a product

containing methyl alcohol crystallizes at first, but this slowly loses weight and, in case the alcohol used was perfectly dry, leaves a pure, white powder.

Calc. for $C_{16}H_{14}O_2NNa$: Na, 7.9%. Found: Na, 7.7%.

The quickest way to get pure sodium compound is to add the calculated quantity of metallic sodium to a solution of the nitroketone in dry benzene and heat. The metal disappears rapidly, and the sparingly soluble derivative separates as a white microcrystalline powder, much less sensitive to atmospheric moisture than previous preparations, and admirably adapted for further transformation. The yield of sodium compound is about 90%. After washing with benzene and dry ether this preparation gave

Calc. for $C_{16}H_{14}O_2NNa$: Na, 7.9%. Found: Na, 7.7%.

The sodium compounds from all sources behaved alike towards water, acids, alcohols, bromine and allyl halides.

In cold water the sodium compound dissolves readily and gives a clear, colorless, very feebly alkaline solution. This soon becomes milky, however, and in less than an hour practically all of the substance is hydrolyzed to sodium hydroxide and nitroketone. Dry alcohols also dissolve large quantities of the metallic derivative. The solutions remain clear and colorless and on evaporation under diminished pressure, they deposit a crystalline sodium compound containing alcohol. The reaction between the sodium compound and acids is much cleaner than that of the metallic derivatives of the simpler nitroparaffins; the result is the same with weak as with strong acids and whether the acid is added to the sodium compound or *vice versa*. The product is an oil that quickly solidifies, and on crystallization gives the calculated quantity of pure nitroketone.

γ -Bromo- γ -nitro- β -phenylbutyrophenone, $NO_2CHBrCH(C_6H_5)CH_2CO-C_6H_5$.—The dry sodium compound was added, gradually, to a well cooled solution of slightly more than one equivalent of dry bromine in chloroform. Reaction is immediate even at the temperature of a freezing mixture. The product was poured into water, the excess of bromine removed with bisulfite, the chloroform layer dried, and freed from chloroform by evaporation under diminished pressure. This left a colorless solid that, on repeated recrystallization from methyl alcohol, gave colorless needles melting at 90° , and thin plates or flat needles that melted at 93° . A mixture of the two substances began to melt at about 70° .

Calc. for $C_{16}H_{14}O_2NBr$: Br, 22.7%. Found (90°): Br, 22.8%; (93°): Br, 22.8%.

It is not possible to make these monobromo derivatives by starting with a methyl alcoholic solutions of the sodium compounds. Such solutions react with almost exactly the same amount of bromine as the dry substance, but the result is always a mixture of nitroketone, with its monobromo and dibromo substitution products, and the amount of dibromo

is considerable even when the solution of the sodium compound is dropped into excess of bromine. It is easy to remove the dibromo derivative from this mixture, but the separation of monobromo derivative and nitroketone is tedious and wasteful. Both needles and plates are very readily soluble in all common organic solvents except ligroin.

γ,γ -Dibromo- γ -nitro- β -phenylbutyrophenone, $\text{NO}_2\text{CBr}_2\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COC}_6\text{H}_5$.—Neither of the monobromo derivatives just described reacts with bromine at low temperatures, but both of them readily dissolve in sodium methylate, and the resulting solutions rapidly decolorize bromine. Both substances give the same product, small, colorless needles, sparingly soluble in alcohol and ether, readily in chloroform. The substance melts at 160 – 162° and begins to decompose freely as soon as melted.

Calc. for $\text{C}_{16}\text{H}_{15}\text{O}_2\text{NBr}_2$: Br, 37.5%. Found: Br, 37.5%.

The same dibromo compound can be made without starting with the monobromo derivatives; it can be prepared far more easily and with a satisfactory yield by starting, either with a solution of the nitroketone in sodium methylate, or with the methyl alcoholic solution of the sodium compound that is obtained when a solution of sodium nitromethane is added to benzalacetophenone. When bromine is dropped into either of these solutions, cooled in a freezing mixture, it disappears as fast as added. The color of the solution at first changes gradually from pale yellow to deep yellow and orange, then becomes lighter again and finally colorless after a little more than one molecule of bromine has been added. At this stage the mixture contains only dibromo compound, nitroketone, and sodium bromide, the play of colors being due to the intermediate formation of the yellow sodium derivative of the monobromo compound and its subsequent removal by bromine. The mixture does not react with any more bromine, but by adding half the original amount of sodium alcoholate, the nitroketone is once more turned into sodium compound and will decolorize an equivalent quantity of bromine. This cycle can be repeated until enough bromine has been added to transform all of the nitroketone into dibromo compound. Sodium bromide and dibromo compound are then filtered off, washed with dilute alcohol and water and recrystallized from chloroform and alcohol. Yield, 80–85%.

The most characteristic property of these γ -bromo derivatives is the ease with which they are reduced. Solutions of the dibromo compound in acetone or alcohol can be boiled for a long time without appreciable loss, but when an equivalent quantity of potassium iodide or potassium cyanide is added to the solution one of the bromine atoms is rapidly replaced by hydrogen and, in the presence of excess of reducing agent, the resulting monobromo compound is more slowly, but completely, reduced to the nitroketone.

γ -Nitro- β -phenyl- α -bromobutyrophenone, $\text{NO}_2\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{CHBrCO}\text{C}_6\text{H}_5$. The procedure used for introducing bromine in the α -position was as follows: A small quantity of bromine was added to a concentrated solution of the nitroketone in chloroform, and the reaction started either by warming on a steam bath or addition of a drop of acetone. The solution was then cooled with running water and treated with bromine until the color showed a slight excess—90 g. of nitroketone dissolved in 150 g. of chloroform reacted with 58 g. of bromine. Excess of bromine, hydrobromic acid, and solvent, were then removed as completely as possible by warming under diminished pressure. The pale yellow oil that remained was dissolved in hot absolute alcohol. This solution, on cooling, slowly deposited large, colorless needles that melted at 100° .

Calc. for $\text{C}_{18}\text{H}_{16}\text{O}_2\text{NBr}$: Br, 22.7%. Found: Br, 22.8%.

Two more substances were obtained from the filtrates. These were formed only in small quantities and were separated with great difficulty. One of these crystallized from alcohol in thin plates and melted at 86° .

Calc. for $\text{C}_{18}\text{H}_{16}\text{O}_2\text{NBr}$: Br, 22.7%. Found: Br, 22.4%.

The total yield of pure monobrom derivatives was 89%. The third product crystallized in prisms or thick needles and melted at 105° . The analyses show that this is a dibromo derivative. This substance constituted only about 4% of the product, its structure has not been determined.

Calc. for $\text{C}_{18}\text{H}_{14}\text{O}_2\text{NBr}_2$: Br, 37.5%. Found: Br, 37.6%.

γ -Nitro- β -phenyl- α -iodobutyrophenone, $\text{NO}_2\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{CHICO}\text{C}_6\text{H}_5$.—Slightly more than one equivalent of potassium iodide was added to each of the α -bromo compounds dissolved in the smallest possible quantity of boiling methyl alcohol. Potassium bromide began to separate almost immediately and a very faint yellow color appeared in the solutions. After boiling for half an hour, the solutions were poured into water. This precipitated pale yellow oils that soon solidified. The product from both bromine compounds was found to be the same. It was purified by crystallization from alcohol from which it separated in pale yellow needles that melted at 123° . The iodine compound is less soluble than either of the bromine compounds and separates much more rapidly from solutions.

Calc. for $\text{C}_{18}\text{H}_{14}\text{O}_2\text{NI}$: I, 32.2%. Found: I, 31.9%.

The most characteristic property of the α -halogen compounds is the ease with which they lose hydrobromic acid when treated with alcoholates, potassium acetate, potassium cyanide, and other feebly alkaline reagents. The product in each case is a trimethylene compound melting at 93° . The properties of this substance will be considered in a later paper dealing with the chemistry of cyclopropane and its derivatives.

γ -Bromo- γ -nitro- β -phenyl- α -bromobutyrophenone, $\text{NO}_2\text{CHBrCH}(\text{C}_6\text{H}_5)\text{CHBrCOC}_6\text{H}_5$.—The α -bromo derivatives are not attacked by bromine, and, owing to the ease with which they pass into trimethylene compounds, it is not possible to transform them into sodium compounds. Further bromination of α -bromo compounds is therefore impossible. The γ -bromo compound, on the other hands, can be brominated by the same procedure that was used for getting α -bromo derivatives. The product obtained by brominating the needles (90°) crystallizes from alcohol in thin needles melting at 130° . It is sparingly soluble in cold alcohol and ether, readily in acetone and chloroform.

Calc. for $\text{C}_{16}\text{H}_{15}\text{O}_2\text{NBr}_2$: Br, 37.5%. Found: Br, 37.6%.

When an alcoholic solution of this dibromo derivative is boiled with potassium iodide the principal product is the α -iodo compound melting at 123° . One of the bromine atoms is, therefore, in the α - and the other in the γ -position. When a similar solution is boiled with zinc dust, one of the products is the trimethylene compound melting at 93° , but the yield is very poor.

γ,γ -Dibromo- γ -nitro- β -phenyl- α -bromobutyrophenone, $\text{NO}_2\text{CBr}_2\text{CH}(\text{C}_6\text{H}_5)\text{CHBrCOC}_6\text{H}_5$.—The γ,γ -dibromo derivative can also be brominated directly, but, in order to start the reaction, it is necessary either to expose the reacting mixture to sunlight or to add to it a drop of acetone. The product crystallized from chloroform in large, lustrous needles that melt at 185° . It is sparingly soluble in ether, alcohol, and cold chloroform, readily in boiling chloroform.

Calc. for $\text{C}_{16}\text{H}_{13}\text{O}_2\text{NBr}_3$: Br, 47.4%. Found: Br, 47.7%.

II. Benzalacetophenone and Nitroethane.

γ -Nitro- β -phenylvalerophenone, $\text{CH}_3\text{CH}(\text{NO}_2)\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COC}_6\text{H}_5$.—The addition of nitroethane was accomplished in exactly the same way as that of nitromethane. As sodium nitroethane is stable on alcoholic solution, the mixture remains colorless throughout the process and, probably because of hindrance due to the methyl group, there is little tendency to form a dimolecular product. When the addition is carried out in a sufficiently concentrated solution in absolute alcohol, a solid sodium compound separates in colorless needles. This, with acids, gives a colorless oil that solidifies very slowly. The solid is a mixture of stereoisomers that have a pronounced tendency to separate from solution as oil and consequently are very hard to separate. Repeated crystallization from dry ether gave very fine needles melting at 72° , and stout needles or plates melting at 100° .

Calc. for $\text{C}_{18}\text{H}_{17}\text{O}_2\text{N}$: C, 72.1%; H, 6.0%. Found (72°): C, 72.0%; H, 6.0%; (100°): C, 72.4%; H, 6.0%.

The reaction is quantitative, but the relative amounts of the two isomers vary with the mode of acidification. Strong acids and low temperatures favor the formation of the higher melting product. That these substances are the two racemic modifications possible because the nitroketone contains two dissimilar asymmetric carbon atoms, is shown by the fact that when either substance is turned into the sodium derivative and this back into the nitroketone, the result is always a mixture of the two.

γ -Bromo- γ -nitro- β -phenylvalerophenone, $\text{CH}_3\text{CBr}(\text{NO}_2)\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COC}_6\text{H}_5$.—As the nitroketone has only one hydrogen replaceable by metals it is not necessary to have either dry sodium compound or even pure ketone for making the γ -bromo derivative. An excellent yield of the substance was obtained by adding the calculated amount of sodium methylate to a hot solution of benzalacetophenone and nitroethane in dry methyl alcohol, allowing this solution to stand for an hour, then cooling it in a freezing mixture and dropping bromine into it until the color became permanent. Much of the product separated during the process. After crystallization from chloroform and alcohol this was obtained in the form of fine needles sparingly soluble in alcohol and ether, readily in chloroform. The melting point is 17° .

Calc. for $\text{C}_{17}\text{H}_{16}\text{O}_2\text{NBr}$: Br, 22.1%. Found: Br, 22.2%.

The alcoholic filtrates contained a second product that also crystallized in needles, but was more soluble in alcohol and melted at 160° .

Calc. for $\text{C}_{17}\text{H}_{16}\text{O}_2\text{NBr}$: Br, 22.1%. Found: Br, 22.3%.

γ -Nitro- β -phenyl- α -bromovalerophenone, $\text{CH}_3\text{CH}(\text{NO}_2)\text{CH}(\text{C}_6\text{H}_5)\text{CO}\text{C}_6\text{H}_5$.—The nitroketones, dissolved in chloroform, readily react with bromine, but, probably owing to the number of stereoisomers formed, no solid product could be isolated. The residue left after removing the solvent, however, reacts with potassium acetate in the manner of these α -bromo compounds and gives two solid trimethylene derivatives.

III. Benzalacetophenone and β -Nitropropane.

The preparation of any considerable quantity of β -nitropropane is a matter of some difficulty. V. Meyer obtained the substance by adding silver nitrite to isopropyl iodide and distilling, but he does not state his yield. Nef, who later prepared it in the same way, states that the yield is very poor. My yields by this method were 5–6 g. of pure nitro compound per 100 g. of isopropyl iodide. After trying various modifications of this method, I finally adopted the following: 100 g. of finely ground silver nitrite are added, in the course of several hours, to a solution of 100 g. of isopropyl iodide in 300 cc. of dry, alcohol-free ether. Each spoonful of solid produces a sensible reaction in the liquid and if the mixture is shaken during the addition or immediately afterwards, the solid cakes;

but if the reaction is allowed to proceed until the temperature begins to fall after each addition, and the mixture is then shaken vigorously, the solid remains as a loose powder. In order to complete the reaction it is necessary either to boil for about 12 hours or to allow the mixture to stand in a dark place for several weeks. The latter gives the better yield. The ethereal layer is filtered, the solid repeatedly extracted with boiling ether, the ether removed from the solutions and the residue separated by fractional distillation. The yield by this method was 12–15 g. of pure nitro compound boiling at 120° per 100 g. of isopropyl iodide.

γ -Methyl- γ -nitro- β -phenylvalerophenone, $\text{CH}_3\text{C}(\text{CH}_3)(\text{NO}_2)\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COC}_6\text{H}_5$.—The addition of a secondary nitro compound to an unsaturated compound was of special interest because the product is necessarily a tertiary nitro compound. The sodium compound resulting from the addition of sodium β -nitropropane to benzalacetophenone therefore cannot rearrange to give the type of sodium compound obtained with nitromethane and primary nitroparaffins. It was found that the reaction goes much more slowly than in the cases previously described—doubtless owing to the hindrance caused by the highly branched chain. In absolute ether and in dry benzene there is scarcely any evidence of reaction. In absolute alcohol the addition starts in the usual way, but the resulting sodium compound is rapidly decomposed by the alcohol, hence the solution becomes increasingly alkaline as the reaction proceeds, and the substance that separates is not a sodium compound but the nitroketone itself. With equivalent quantities of benzalacetophenone and sodium β -nitropropane the yield is insignificant, because both sodium nitropropane and the nitroketone are slowly decomposed by excess of sodium alcoholate. In this case, therefore, the best results are obtained by using only a small quantity of sodium alcoholate as condensing agent. The following procedure gave excellent results: equivalent quantities of unsaturated ketone and nitro compound were dissolved in enough absolute methyl alcohol to keep the ketone in solution in the cold, 5 drops of a strong sodium methylate solution were then added, and the mixture set aside in a securely corked flask. The solution slowly turned yellow, and a colorless solid began to separate in the course of a few days. This continued to increase for several weeks, at the end of which the reaction was complete. The product was purified by recrystallization from a mixture of chloroform and alcohol. Yield, 92%.

Calc. for $\text{C}_{18}\text{H}_{19}\text{O}_4\text{N}$: C, 72.7%; H, 6.4%. Found: C, 72.8%; H, 6.6.

The nitroketone is sparingly soluble in alcohol and ether, readily in benzene and in chloroform. It melts at 167° . The difference in solubility and melting point between this substance and the nitroketones

previously described is conspicuous. The melting points of primary and secondary nitroketones as well as those of the halogen substitution products that still have hydrogen in combination with the carbon that holds the nitro group, are relatively low, while all of the isomeric substitution products that no longer have hydrogen in this position melt much higher and are far less soluble.

Nitromethylphenylvalerophenone shows no tendency to form a metallic derivative. Its solubility in dilute sodium alcoholate is no greater than in alcohol. It is readily soluble in concentrated alcoholate but the process is accompanied by extensive decomposition. The solution contains benzalacetophenone, sodium β -nitropropane, sodium nitrite, and other products of unknown structure. Metallic sodium slowly attacks a solution of the nitroketone in dry benzene but in this case also, the result is not the formation of a metallic derivative—sodium nitropropane and a more complex sodium compound are precipitated while benzalacetophenone and other substances remain dissolved in the benzene.

γ -Methyl- γ -nitro- β -phenyl- α -bromovalerophenone, $\text{CH}_3\text{C}(\text{CH}_3)(\text{NO}_2)\text{CH}(\text{C}_6\text{H}_5)\text{CHBrCOC}_6\text{H}_5$.—When a solution of the nitroketone in chloroform is treated with bromine in the usual way it gives two isomeric monobromo derivatives that are easily separated by crystallization from chloroform and alcohol. One of these crystallizes in thin, diamond-shaped, plates that are sparingly soluble in boiling alcohol and in cold chloroform, and melt at 165° . The other bromine compound is readily soluble in hot alcohol and crystallizes in stout prisms that melt at 125° .

Calc. for $\text{C}_{18}\text{H}_{18}\text{O}_2\text{NBr}$: Br, 21.3%. Found (155°): Br, 21.6%; (125°): Br, 21.4%.

Summary.

1. The metallic derivatives of nitroparaffins combine with unsaturated ketones to form metallic derivatives of nitroketones.
2. The addition takes place in such a manner that the metal goes to the carbonyl oxygen and the nitroparaffin residue to the β -position; but unless the result is a tertiary nitro compound the product immediately rearranges to a metallic derivative in which the metal is in combination with the nitro group.
3. Bromine reacts with the metallic derivatives of nitroketones and replaces hydrogen in the α -position to the nitro group; while the hydrogen in the α -position to carbonyl is replaced in the reaction between bromine and the free nitroketones.

From the halogen derivatives of the nitroketones in which the halogen is α to carbonyl, it is easy to get cyclopropane derivatives that have a nitro group in combination with one of the carbon atoms in the ring.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE RATES OF CONVERSION OF THE STEREOISOMERIC CINCHONA ALKALOIDS INTO THEIR TOXINES.¹

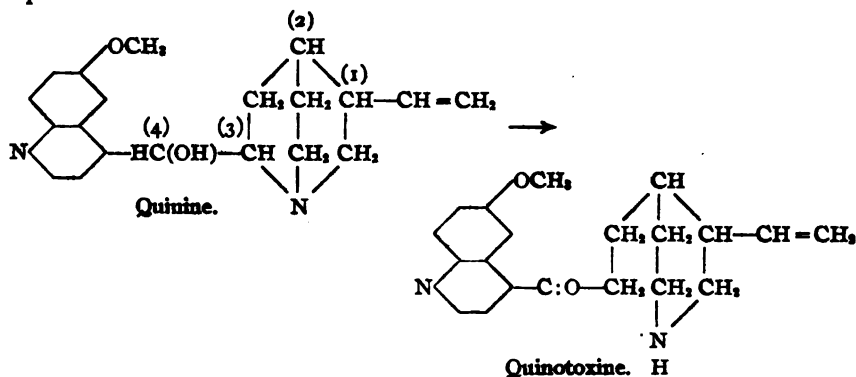
(ON CATALYSES WITH WEAK ACIDS. IX.)

By H. C. BIDDLE.

Received February 1, 1916.

1. Introduction.

The stereoisomeric relation between cinchonine and cinchonidine renders of interest the comparative rates of conversion of these two alkaloids into cinchotoxine. Like interest centers about the rates of conversion of quinine and quinidine into quinotoxine. The relation between each pair of alkaloids and its corresponding toxine may be graphically represented as follows:



Quinidine, it may be noted, is stereoisomeric with quinine. Cinchonine and cinchonidine are also stereoisomeric and these compounds and cinchotoxine differ from quinine, quinidine and quinotoxine in constitution only in that they have hydrogen in place of the methoxy group.

Of importance in the consideration of these alkaloids is the question as to the exact differences in stereoisomerism. In the formulas of the two groups of alkaloids given there are present in each case, as is seen, four asymmetric carbon atoms. As has been shown from the numerous investigations of Skraup, König, and Rabe² both in the case of quinine and quinidine and in that of cinchonine and cinchonidine; two (1 and 2) of the three asymmetric carbon atoms within the bridged ring³ do not differ in configuration. The third asymmetric carbon atom (3) within

¹ THIS JOURNAL, 37, 2088 (1915) and preceding articles.

² *Ann.*, 373, 91 (1910). Through an oversight, Rabe was previously (THIS JOURNAL, 37, 2083 (1915)) incorrectly represented as attributing the stereoisomerism of cinchonine and cinchonidine solely to the spatial arrangement about the third asymmetric carbon atom (3) within the ring.

³ According to a suggestion of König's a bridged ring of this type may be designated as a quinuclidine ring. *Ber.*, 37, 3244 (1904); 38, 3049 (1905).

the ring, however, presents the possibility of an antipodal spatial arrangement and, as Rabe concludes from the relation of desoxycinchonine to desoxycinchonidine and of desoxyquinine to desoxyquinidine, such antipodal configuration actually exists about this carbon atom in the case of each of the two pairs of isomers. But apparently conflicting evidence arises from the fact that both cinchonine and cinchonidine are oxidized to the same cinchoninone and quinine and quinidine under like conditions yield the same quinoninone. This finds reasonable explanation, however, as Rabe clearly shows in the keto-enol tautomerism presented by the oxidation product. This tautomerism points to a dynamic equilibrium existing between four forms (two keto, two enol). The explanation is upheld by the phenomena of mutarotation shown by the salts of cinchoninone and those of quinoninone.

As to the remaining asymmetric carbon atom (4), Rabe calls attention to the fact that experimental evidence is insufficient to draw a definite conclusion here regarding the configuration presented in the case of either pair of isomers. More recently Kaufmann and Huber¹ have succeeded in reducing hydrocinchoninone to a mixture of hydrocinchonine (over 50%) and of hydrocinchonidine (about 10%). While not advancing this as any evidence regarding the configuration about the fourth asymmetric carbon atom, these investigators conclude that hydrocinchoninone itself cannot be a mixture of two optical isomers in equivalent quantities. Definite evidence regarding the configuration about this asymmetric carbon atom must, consequently, await further investigation.

In the study of the conversion of quinine and quinidine into quinotoxine which has been carried out in this laboratory,² it has been shown that the same laws obtain as in the corresponding conversion of cinchonine and cinchonidine into cinchotoxine. The rates of conversion as in the latter case are directly proportional to the concentration of the univalent alkaloid ion and furthermore these rates are a linear function of the concentration of the undissociated organic acid, that is to say, the increments in speed are directly proportional to the increasing concentration of the undissociated organic acid.³ In comparing the conversion rates of quinine and quinidine, however, it was noted that the speeds in cases under like conditions approach a common value. This raised the question as to whether the slightly different rates previously observed under like conditions in the case of cinchonine and cinchonidine⁴ were real or only

¹ *Ber.*, 46, 2913 (1913).

² Unpublished thesis of H. N. Massey.

³ In view of the extraordinary nature of the catalysis of the cinchona alkaloids and its dependence upon the univalent ion, the study is being extended to the alkyl cinchona salts in which, in one case, the alkyl radical is attached to the quinoline nitrogen and, in the other, to the quinuclidine nitrogen.

⁴ Biddle and Butzbach, *THIS JOURNAL*, 37, 2082 (1915).

apparent. A reconsideration of these rates has shown that in the case of the two alkaloids, the speed of change to a mean rotational value under like conditions approaches identity within the limits of experimental error, and that furthermore this mean rotational value probably represents the true rotation of the completely converted, *pure, nonracemized* cinchotoxine.

2. The Optical Rotation of Cinchotoxine.

As can readily be shown from a consideration of the equations employed in the calculation of reaction rates, slight variations in the rotatory values assigned to cinchotoxine would suffice to account for slight, but appreciable errors. In comparing reaction rates of stereoisomeric alkaloids it is, consequently, of importance to fix the rotatory value of the cinchotoxine with some degree of definiteness. The rotation (Ventzke degrees) observed by Biddle and Rosenstein¹ in a decimeter length of a 0.1 molal solution of cinchotoxine in 1.7 molal acetic acid at 18°, was 2.08° and in 3.2 molal acetic, was 2.70°. The value later noted by Biddle and Brauer² under like conditions in concentrations of acetic acid varying from 0.4 to 1.0 molal was 3.00°. This last value was employed by them in all their calculations.

The rotatory power of cinchotoxine salts has been studied by several investigators whose results are not in full agreement. Some preliminary measurements were made by Howard³ in 1872. Thereafter, Hesse⁴ secured definite measurements of the oxalate which were subsequently confirmed by Roques.⁵ The results obtained by the last two investigators are given in Table I, the specific rotations being reduced to Ventzke degrees and calculated for 0.1 molal concentrations of the alkaloid.

TABLE I.

No.	Investigator.	Substance.	Concentration of alkaloid used.	Rotation referred to alkaloid as 0.1 molal.
1	Hesse	Cinc. oxalate, $(C_{19}H_{23}N_2O)_2C_2H_2O_4 + 3H_2O$ (from cinchonine)	0.0546	2.40°
2	Hesse	Cinc. oxalate (from cinchonidine)	0.0546	2.38°
3	Hesse	Cinc. oxalate + 2 mols. H_2SO_4	0.0546	2.72°
4	Roques	Cinc. + 2 mols. HCl	0.0340	2.434°

The salts employed by Hesse were prepared from amorphous cinchotoxine; those of Roques, from the crystallized base. Later, Roques more carefully prepared his material and from salts of the more highly purified base obtained a rotation higher than that previously observed and which is in close agreement with the value obtained by Biddle and

¹ THIS JOURNAL, 35, 421 (1915).

² *Ibid.*, 37, 2065 (1915).

³ *J. Chem. Soc.*, 25, 102 (1872).

⁴ *Ann.*, 166, 277 (1873); 178, 262 (1875).

⁵ *Compt. rend.*, 120, 1170 (1895); *Bull. soc. chim.*, [3] 13, 1005 (1895).

Brauer. In Table II are presented for comparison the values for equivalent quantities of the alkaloid, reduced in all cases to Vantzke degrees. Measurements given in both tables were in general made at temperatures ranging from 15° to 18°.

TABLE II.

No.	Investigator.	Substance.	Concentration of alkaloid used.	Rotation referred to alkaloid as 0.1 molal.
1	Roques	Cinc. + 2 mols. HCl (from cinchonine)	0.034	3.20°
2	Roques	Cinc. + 2 mols. HCl (from cinchonidine)	0.034	3.26°
3	Roques	Cinc. + 4 mols. HCl (from cinchonine)	0.034	3.02°
4	Roques	Cinc. + 4 mols. HCl (from cinchonidine)	0.034	2.95°
5	Roques	Cinc. oxalate, $(C_{19}H_{23}N_3O)_2C_2H_2O_4 + 4H_2O$ (from cinchonine)	0.0296	3.16°
6	Roques	Cinc. oxalate (from cinchonidine)	0.0296	2.98°
7	Roques	Cinc. nitrate, $C_{19}H_{23}N_3O.HNO_3$	0.028	3.04°
8	Biddle and Brauer	Cinc. + 4 mols. to 10 mols. acetic acid	0.10	3.00°

It is of interest to note in this connection that the rotations of equivalent solutions of cinchotoxine are practically identical irrespective of whether the base is derived from cinchonine or cinchonidine. Both Howard and Hesse earlier observed the same fact when dealing with impure cinchotoxine. As Roques points out, this leads to the conclusion that the impurity arising in cinchotoxine during the process of formation is identical irrespective of the source from which the base is derived.

The final results obtained, as Roques indicates, are of further interest in that they point to the apparent correctness of an hypothesis first postulated by Howard, but which from his data he was unable to establish, *viz.*, that the rotatory power of cinchotoxine should be the arithmetical mean of those of cinchonine and cinchonidine.

Furthermore, as is seen, the solutions given in Table II, even though presenting considerable variation in concentration of H^+ ion, yet differ little in rotation. It seems reasonable, consequently, to assume, as Biddle and Brauer have done, that rotational variations due to this cause are in this case negligible in calculating the reaction rates.

3. The Conversion Rates of Cinchonine and Cinchonidine to Cinchotoxine.

From the studies of Hesse and Roques it seems evident then that in the process of the conversion of cinchonine or cinchonidine into cinchotoxine some other reaction takes place to a slight extent with the result that the unpurified product gives a rotation lower than that of pure cinchotoxine. Such a side reaction would to some extent affect the quantitative data employed in studying the relative speed of conversion of the two alkaloids into cinchotoxine. The error, though naturally slight, would lead to an apparent increase in the speed of conversion of the cinchonine and an apparent decrease in that of the cinchonidine.

In order that a direct comparison might be made with regard to the simultaneous conversion of the two alkaloids under the same conditions, experiments were carried on with equivalent mixtures of cinchonine and cinchonidine dissolved in an excess of acetic acid. Assuming that the two alkaloids do not mutually interfere with each other, opportunity is thus afforded to observe the variations in rotation during the course of the reaction. In view of the fact that solutions of the cinchona alkaloids become discolored much less rapidly in the absence of the oxidizing influence of air, the heating was carried out in sealed tubes which had been exhausted until the pressure was reduced to 20 mm. The removal of the air was of additional advantage in that changes in rotation during equal time intervals were found to be to a considerable extent decreased thereby. Both these facts point to the conclusion that the air is one of the factors at least in part responsible for deviations in these reactions.

The results of an experiment are given in Table III.

TABLE III.

Cinchonine and cinchonidine, each 0.05 molal. Acetic acid, 1.7 molal. Temp., 99.4° ($\pm 0.2^\circ$).

Time.....	0 hr.	4 hrs.	6 hrs.	23 hrs.	25 hrs.	52 hrs.	111 hrs.	335 hrs.
Rotation ¹	3.21°	3.11°	3.00°	2.55°	2.55°	2.25°	1.75°	1.00°

A consideration of this table is instructive. As is seen, there is a gradual but continuous fall in rotation to the close of the period, even though the conversion to cinchotoxine may, for all practical purposes, be regarded as complete before the close of the first fifty hours.

If now the rotation of the cinchotoxine were assumed to be that of the sixth reading, 2.25°, the gradual fall in rotation observed cannot be accounted for in case the rate of conversion of the cinchonine either exceeds or equals that of cinchonidine. The observed readings might be obtained, however, as can be shown by calculation, if the conversion rate of the cinchonidine slightly exceeded that of its isomer. But the assumption of a rotational value of 2.25° in the above experiment, fails entirely to explain the continued fall in rotation after the conversion to cinchotoxine is practically complete.

If, on the other hand, the rotatory power of cinchotoxine is the arithmetical mean of those of the other two alkaloids, then, as will be evident, the observed rotations should remain constant throughout the conversion, unless the rate of conversion of one alkaloid exceeds that of the other, or unless such constancy is disturbed by side reactions. The direction of deviations in rotation, if dependent upon difference in rate, would naturally be determined by which of the two alkaloids presented the more rapid rate of conversion. The decrease in rotation observed might at first glance seem to favor the conclusion that the rate of conversion

¹ Readings made in this and the following experiments at 18°.

of cinchonine exceeds that of cinchonidine as previously reported. The fall in rotation would in such case, however, not be continuous, but after attaining a maximum value would return to the original reading. Thus, for example, the final reading in Table III should, under these conditions, practically equal the initial reading of 3.21° .

If, then, we assume that the specific rotation of cinchotoxine is the arithmetical mean of those of the other two alkaloids, the conclusion must be reached that the continuous fall in rotation must be due to a secondary reaction, or reactions, the nature of which will be considered later in this paper.

It will be noted from Table III that the fall in rotation amounts only to about 0.2° in six hours. If, consequently, the rates of conversion of cinchonine and cinchonidine into cinchotoxine were studied during the early part of the reaction under the given conditions, the error introduced by this deviation may be reduced to a minimum. With this in view, the conversion rates of the two alkaloids were remeasured simultaneously for one concentration of acetic acid under precisely the same experimental conditions. The mode of procedure had the additional advantage of eliminating other slight errors which may have arisen in previous determinations from differences in manipulation due to the personal equation, since the former measurements for cinchonine were made by one experimenter and those for cinchonidine by another. The solutions were heated, as in the previous experiment, in sealed tubes evacuated to a pressure of 20 mm. The arithmetical mean of the initial readings of the two alkaloids is chosen as the rotation of the corresponding cinchotoxine solution. The results are recorded in Tables IV and V.

TABLE IV.

Cinchonine, 0.1 molal; Acetic acid,
1.7 molal; $L = 1.0$ dm.; $T =$
99.4 ($\pm 0.2^\circ$).

<i>t.</i>	<i>a.</i>	<i>K</i> ₁	<i>K</i> ₂
0 hr.	20.9
0.5 hr.	19.5	0.0716	0.0716
1.5 hrs.	17.1	0.0701	0.0694
2.5 hrs.	14.9	0.0722	0.0752
3.5 hrs.	12.9	0.0749	0.0818
4.5 hrs.	11.8	0.0699	0.0525
5.5 hrs.	10.2	0.0736	0.0900
α hrs.	3.25

Mean, 0.0721 0.0734

TABLE V.

Cinchonidine, 0.1 molal; Acetic acid,
1.7 molal; $L = 1.0$ dm.; $T =$
99.4 ($\pm 0.2^\circ$).

<i>t.</i>	<i>a.</i>	<i>K</i> ₁	<i>K</i> ₂
0 hr.	-14.4
0.5 hr.	-13.0	0.0716	0.0716
1.5 hrs.	-10.6	0.0701	0.0694
2.5 hrs.	-8.6	0.0692	0.0678
3.5 hrs.	-6.7	0.0712	0.0759
4.5 hrs.	-5.3	0.0699	0.0658
5.5 hrs.	-4.0	0.0703	0.0717
α hrs.	3.25

Mean, 0.0704 0.0704

In the light of the facts already discussed, a consideration of the results given in Tables IV and V leads to the unavoidable conclusion that the rates of conversion of cinchonine and cinchonidine to cinchotoxine are identical within the limits of experimental error, providing we assume

that the specific rotation of cinchotoxine is the arithmetical mean of the corresponding rotations of the other two alkaloids. A reaction rate *apparently* slightly greater in the case of the cinchonine was to be expected. Small differences in rate, if at all existent, can be detected only by more refined experimental methods. The same principle obtains apparently as well with respect to the rates of conversion of quinine and quinidine into quinotoxine.

In order that confirmatory evidence might be obtained regarding the comparative reaction rates of the two alkaloids, recourse was had to a former method of measurement. Unfortunately, the procedure of Biddle and Rosenstein based upon the separation of the alkaloid from cinchotoxine by means of ammonium hydroxide in the presence of an ammonium salt was not readily applicable, since cinchonidine is considerably more soluble under these conditions than is cinchonine. A modification of the earlier ether extraction method, however, proved of service. The cinchotoxine was weighed in each case as such, being freed from traces of unchanged alkaloid by re-resolution in *absolute* ether in which both cinchonine and cinchonidine are difficultly soluble. While the method naturally does not present the accuracy¹ of that dependent upon optical rotation, the results obtained fully agreed with those already given as to the identity of the two rates of conversion.

We must conclude then, that *in the conversion of stereoisomeric cinchona alkaloids into their toxins as represented on the one hand by cinchonine and cinchonidine to cinchotoxine and on the other by quinine and quinidine to quinotoxine, the rates of conversion of stereoisomers, as indicated by the rates of approach to a position of mean optical rotation, are identical within the limits of experimental error.*

4. Cause of the Diminishing Rotation.

Roques accounted for the low specific rotations first observed in the study of cinchotoxine by assuming the presence of a common impurity irrespective as to whether the toxine was derived from cinchonine or from cinchonidine. What the nature of this impurity was, however, he did not venture to suggest.

In considering the data presented in Table III, one is struck with the fact that the fall in rotation is *continuous* throughout the entire period of the reaction, regardless as to whether the solution at any moment contained three optically active substances or the cinchotoxine alone. While under ordinary conditions the oxidizing influence of the air may have some influence upon this change, it is obvious that under the ex-

¹ It is to be regretted that apart from the data presented by optical rotation a quantitative method is lacking which would enable us to measure with precision small differences of reaction rate. Some such method is to be desired in order that the comparative conversion rates of stereoisomers may be subjected to more rigid examination.

perimental conditions employed such influence is totally inadequate to account for the results obtained. Indeed, in view of the facts presented only one reasonable explanation can be offered and that is one dependent upon the slow racemization of the optically active substances present. In the protracted heating of the cinchona alkaloids under the conditions of the experiment, partial racemization might naturally be expected. In the case of cinchonine and cinchonidine this racemizing action might extend to any one or all of the four asymmetric carbon atoms (see graphic formulae at beginning of this paper); in the case of cinchotoxine it would naturally be confined to carbon atoms one and two.

A slow racemizing action of this kind fully accords with the facts observed. Thus, it accounts for the supposed impurity which Roques thought was derived indifferently either from cinchonine or cinchonidine, since, as he noted, both these alkaloids were converted under similar conditions to a cinchotoxine of like low rotation. It explains further the divergent specific rotations of cinchotoxine given in the literature and indicates why extraordinary care was found necessary to obtain a cinchotoxine of high rotation.

As a result of this racemizing influence the reaction rates obtained by Biddle and Brauer for cinchonine are a little high and those given by Biddle and Butzbach for cinchonidine are a little low. These factors, however, materially affect only the comparative rates of conversion of the two alkaloids. The influence upon the data establishing the two principles, *viz.*, the action of univalent alkaloidal ion and that of the concentration of the undissociated organic acid upon the reaction, is consequently negligible.

Summary.

1. The specific rotatory power of cinchotoxine closely approaches, if it does not equal, the arithmetical mean of the corresponding rotatory powers of the isomeric cinchonine and cinchonidine.

2. In the conversion of the two alkaloids into the common toxine under the influence of an organic acid the rotational values are subject to a slight but continuous error, due to a partial racemization of the alkaloids concerned. The effect of this error upon the reaction rates calculated is that those obtained for cinchonine will invariably be a little high and those for cinchonidine will be a little low.

3. In the conversion of stereoisomeric cinchona alkaloids into their toxines as represented on the one hand by cinchonine and cinchonidine to cinchotoxine and on the other by quinine and quinidine to quinotoxine, the reaction rates, or the rates of approach to a position of mean optical rotation, are identical within the limits of experimental error.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JAMES MILLIKIN UNIVERSITY.]

ALKYL CYANOACETIC ACIDS.

By JOHN C. HESSLER.

Received February 3, 1916.

This paper describes work done, under the writer's direction, by three students, Mr. Thomas B. Magath, Mr. Fred F. Joel, and Miss Margaret C. Hessler. It includes the preparation of several new alkyl cyanoacetic acids, their salts and other derivatives. In this work caustic potash dissolved in methyl alcohol has been used for the saponification of the dialkyl cyanoacetic esters, with excellent results. Finally there is given a description of the benzylation of cyanoacetic ethyl ester in methyl alcohol solution; the dibenzylated derivative is shown to be the methyl, rather than the ethyl ester.

Dimethylcyanoacetic Acid, $(\text{CH}_3)_2\text{C}(\text{CN})\text{COOH}$.—The acid was made from 8.7 g. of its ethyl ester¹ by treatment with a solution of 9 g. of potassium hydroxide in 100 cc. of absolute methyl alcohol. The mixture was kept cool by means of running water and was allowed to stand overnight. Water was then added and the solution was acidified with dilute sulfuric acid. The acid solution was extracted three times with ether and the ether solution was washed five times with water and dried, rapidly, three times with fused calcium chloride. Distillation of the ether left a thick, slightly yellow liquid; this distilled at 132–135° under 12 mm. The distillate weighed 2.5 g.; it crystallized at once when disturbed. The crystals melted at 57° after being dried *in vacuo* over concentrated sulfuric acid.

The silver salt of dimethylcyanoacetic acid was made from the aqueous solution of the acid and freshly precipitated silver carbonate. The mixture was heated with a reversed condenser for 4–5 hours on a boiling water bath; it was then filtered and the filtrate was concentrated on the water bath. The silver salt came out in long, fine crystals.

Calc. for $\text{C}_4\text{H}_6\text{NO}_2\text{Ag}$: Ag, 49.09. Found: Ag, 49.20.

The barium salt was made from the aqueous solution of the acid and powdered barium carbonate. The mixture was heated on the boiling water bath for 2 hours and filtered hot. It was concentrated and then allowed to evaporate in the open air. After 4 weeks the barium salt crystallized out as long prisms; these were very readily soluble in water.

Calc. for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_4\text{Ba} \cdot 18\text{H}_2\text{O}$: Ba, 13.47. Found: Ba, 13.56.

Diethylcyanoacetic Acid, $(\text{C}_2\text{H}_5)_2\text{C}(\text{CN})\text{COOH}$.—The diethylcyanoacetic ethyl ester was made as already described.² Then 42.5 g. of it were treated with 28 g. caustic potash dissolved in 300 cc. of methyl

¹ THIS JOURNAL, 35, 990–994 (1913).

² *Am. Chem. J.*, 22, 171 (1899); also Hadley, THIS JOURNAL, 34, 925 (1912).

alcohol. The mixture stood overnight. It was treated with 2 liters of water and dilute sulfuric acid was added until the solution had an acid reaction. The acid was extracted with ether as in the case of dimethylcyanoacetic acid. It weighed 31 g. and melted at 66° after it had been dried on a clay plate. The melting point previously reported was 57° ,¹ but in this case the acid had been made by saponification with concentrated hydrochloric acid in a sealed tube.

The silver salt was made by the treatment of the acid with a slight excess of aqueous ammonia, removal of the excess of ammonia over sulfuric acid *in vacuo*, and addition of an excess of aqueous silver nitrate. It was a bulky, white precipitate.

Calc. for $C_7H_{10}NO_3Ag$: Ag, 43.55. Found: Ag, 43.41.

The barium salt resulted from the boiling of the acid with water and powdered barium carbonate. The mixture was filtered while hot and was concentrated on a boiling water bath. The salt came out in the form of fine needles; it was analyzed air dry.

Calc. for $C_{14}H_{20}N_2O_4Ba$: Ba, 32.85. Found: Ba, 32.39.

The lead salt was made from the acid and powdered lead carbonate; it crystallized out when its solution was concentrated on the water bath. The salt forms flat, flaky crystals that are somewhat soluble in cold water, and very soluble in hot water. The salt was dried on a clay plate for analysis.

Calc. for $C_{14}H_{20}N_2O_4Pb$: Pb, 42.50. Found: Pb, 42.36.

The calcium salt was made by the method used for the barium salt. It came out as long needles when its solution was concentrated to a small volume. It was analyzed air dry.

Calc. for $C_{14}H_{20}N_2O_4Ca \cdot 3H_2O$: Ca, 10.69. Found: Ca, 10.65.

The strontium salt was obtained as long, soluble prisms.

Calc. for $C_{14}H_{20}N_2O_4Sr \cdot 3H_2O$: Sr, 20.77. Found: Sr, 20.49.

The cadmium salt was formed as flat, irregular plates when its solution was concentrated.

Calc. for $C_{14}H_{20}N_2O_4Cd \cdot 3H_2O$: Cd, 25.17. Found: Cd, 24.84, 24.80.

The copper salt was made from freshly prepared basic copper carbonate and the acid. The copper carbonate was obtained from copper sulfate and sodium carbonate solutions; it was washed by decantation. The copper salt separated from its concentrated solution as rectangular, bright green crystals. It was dried on a clay plate.

Calc. for $C_{14}H_{20}N_2O_4Cu \cdot 3H_2O$: Cu, 15.99. Found: Cu, 16.05, 16.30.

Preparation of Propylcyanoacetic Ethyl Ester,
$$\begin{array}{c} C_2H_5 \\ \diagup \\ H-C(CN)COOC_2H_5 \end{array}$$

¹ Hesse, *Am. Chem. J.*, 18, 746 (1896).

—Propylcyanoacetic ester was made from 50 g. cyanoacetic ester in 100 cc. of absolute alcohol, 10.2 g. of sodium in 250 cc. of absolute alcohol, and 80 g. (one gram equivalent = 75 g.) of normal propyl iodide. The propyl iodide was added as soon as the sodium salt of the cyanoacetic ester began to be precipitated. The solution became hot; the final temperature was 65°.

The mixture was left overnight in a flask protected by a calcium chloride tube and became neutral to litmus. The alcohol and excess of propyl iodide were distilled off on a paraffin bath, the residue was dissolved in water, and the solution was extracted twice with ether. The ether solution was washed five times with water and dried with fused calcium chloride. When the ether was distilled, the crude ester was obtained; it boiled at 117–130° under 24 mm. Yield, 51.5 g.

Propylcyanoacetic Acid and Its Salts.—The crude ester, containing both the monopropyl- and the dipropylcyanoacetic esters, was shaken twice, in ether solution, with an excess of 10% sodium hydroxide solution. The alkaline solution was separated from the ether, acidified with dilute sulfuric acid and extracted three times with ether. The propylcyanoacetic acid obtained weighed 24.9 g. The ether solution neutral to sodium hydroxide contained the dipropylcyanoacetic ester. This will be described later.

a. Silver Salt.—The ammonium salt of the acid was made by treatment of the acid with ammonia water and the removal of the excess of ammonia over concentrated sulfuric acid, *in vacuo*. Silver nitrate in slight excess was then added. The heavy, white precipitate of silver salt was filtered off and dried. A silver determination by ignition resulted as follows:

Calc. for $C_4H_7NO_2Ag$: Ag, 45.95. Found: Ag, 46.52.

b. Barium Salt.—The barium salt was made from the acid, water, and powdered barium carbonate. This mixture was heated several hours on a boiling water bath; the excess of barium carbonate was then filtered off and the filtrate was allowed to stand *in vacuo* over sulfuric acid. The salt crystallized in almost white plates.

Calc. for $C_{12}H_{15}N_2O_4Ba$: Ba, 35.21. Found: Ba, 35.23.

c. Pure propylcyanoacetic ester was made from the silver salt and an excess of ethyl iodide. The mixture was heated gently under a reflux condenser and then distilled. Boiling point 218–219° under 755 mm. Sp. gr. 0.972 at 32°.

Dipropylcyanoacetic Ethyl Ester.—The ether solution neutral to 10% sodium hydroxide was distilled under 21–23 mm. and gave the dipropyl ester, boiling at 129–132°. The amount obtained was 17.8 g., out of the original 51.5 g. of crude ester. Sp. gr. (Westphal) 0.93 at 26°.

Dipropylcyanoacetic Acid.—Dipropylcyanoacetic ester was treated with three times the theoretical amount of potassium hydroxide dissolved in pure methyl alcohol. The mixture stood overnight; it was then poured into much water, acidified with dilute sulfuric acid, and extracted three times with ether. After the ether solution had been washed and dried, the ether was distilled; the acid remained. When left several days *in vacuo* over sulfuric acid it did not crystallize. However, when water was added the acid crystallized in rhombic prisms. When dried on a clay plate the crystals melted at 41° . Over sulfuric acid *in vacuo* the crystals lost water and left a syrupy liquid. After 5 days the results were as follows:

Calc. for $C_9H_{14}NO_2 \cdot H_2O$: H_2O , 9.62. Found: H_2O , 9.68

The silver salt was made from the ammonium salt, as in the case of the silver salt of monopropylcyanoacetic acid. A silver determination was first made in the case of the air dried salt.

Calc. for $C_9H_{14}NO_2Ag \cdot H_2O$: Ag, 36.70. Found: Ag, 36.69.

The salt lost its water of hydration when dried *in vacuo* over sulfuric acid.

Calc. for $C_9H_{14}NO_2Ag$: Ag, 39.13. Found: Ag, 38.82.

Isobutylcyanoacetic Ethyl Ester, $\begin{array}{c} C_4H_9 \\ \diagup \\ C(CN)COOC_2H_5 \\ \diagdown \\ H \end{array}$ —The crude

ester was prepared by the Conrad-Limpach reaction, as in the case of the propyl derivative. The yield was 52.7 g. from 50 g. of cyanoacetic ester. It was distilled in three fractions under a pressure of 35–42 mm.

I. Up to 127° , 11.5 g. II. 127 – 132° , 36.9 g. III. 133 – 185° , 4.3 g.

Isobutylcyanoacetic acid was made by treatment of the crude ester once with 5% sodium hydroxide solution (no ether was used) and twice with 10% sodium hydroxide, the first time for one or two minutes, the second time for one and half hours. After the last treatment the unchanged diisobutylcyanoacetic ester was removed by means of ether. The sodium hydroxide solution was then acidified with dilute sulfuric acid, extracted with ether, and the ether solution dried rapidly with calcium chloride. The yield of acid was 20.5 g. This represents 24.6 g. of ester, or 46.6% of the total yield of crude ester.

The silver salt was made from 17 g. of the acid, by means of the ammonium salt. Yield, 23.7 g. It was an almost white powder after it had been dried on a clay plate.

Calc. for $C_7H_{10}NO_2Ag$: Ag, 43.54. Found: Ag, 43.11.

The barium salt was made when the acid, water and powdered barium carbonate were heated on a boiling water bath. It crystallized in long, white needles when its solution stood in a desiccator over sulfuric acid.

Calc. for $C_{14}H_{20}N_2O_4Ba \cdot 2H_2O$: Ba, 30.51. Found: Ba, 30.36.

Pure isobutyrcyanoacetic ethyl ester was made from the silver salt of the acid and an excess of ethyl iodide. Boiling point $223-224^{\circ}$ under 755 mm. Sp. gr. 0.958 at 35° C.

Diisobutyrcyanoacetic Ethyl Ester.—The part of the crude isobutyrcyanoacetic ester that was neutral to sodium hydroxide solution was taken up with ether and the ether solution was washed with water and dried with calcium chloride. The yield of the diisobutyl ester was 28.1 g., or 53.3% of the crude ester. The boiling point was $245-250^{\circ}$ under 755 mm. Sp. gr. (Westphal) 0.915 at 31° .

Diisobutyrcyanoacetic acid was made from its ester by the action of potassium hydroxide dissolved in methyl alcohol. After the acid had been dried *in vacuo* over sulfuric acid it melted at 82° . Yield, 20 g. from 23.7 g. of the distilled ester.

The silver salt was prepared through the ammonium salt. It formed a bulky, white precipitate.

Calc. for $C_{11}H_{13}NO_3Ag$: Ag, 35.52. Found: Ag, 35.71.

Derivatives of Isoamylcyanoacetic Acid.

a. Copper Salt.—Isoamylcyanoacetic acid was prepared as described in an earlier paper.¹ It was converted into the ammonium salt and the solution was treated with a solution of copper sulfate. The copper salt came out as a blue, crystalline precipitate. It was analyzed air dry.

Calc. for $C_{10}H_{21}N_2O_4Cu \cdot 7H_2O$: Cu, 12.78. Found: Cu, 12.39.

When the salt was dried *in vacuo* over sulfuric acid, it became green.

b. Barium Salt.—The barium salt resulted when the acid, water and powdered barium carbonate were heated together. The salt crystallized from its concentrated, aqueous solution as tufts of white needles.

Calc. for $C_{10}H_{21}N_2O_4Ba \cdot 2H_2O$: Ba, 28.48. Found: Ba, 28.06.

c. Acid Chloride and Anilide.—Isoamylcyanoacetic acid chloride resulted as a colorless liquid when the acid and phosphorus pentachloride (a slight excess) were heated together. The phosphorus oxychloride was distilled *in vacuo*. When the acid chloride was treated with an excess of concentrated ammonia water, the acid amide was produced. It melted at 142° .²

When the acid chloride was treated with aniline, the acid anilide was formed. This separated from alcohol as balls of needle-shaped crystals melting at 102° .

Calc. for $C_{14}H_{19}ON_2$: N, 12.17. Found: N, 12.47.

Diisoamylcyanoacetic Acid and Its Derivatives.

a. Preparation of the Acid.—The diisoamylcyanoacetic ester² that was used in the preparation of the acid boiled at $158-159^{\circ}$ under 16 mm.

¹ THIS JOURNAL, 35, 993 (1913).

² *Ibid.*, Loc. cit.

It was saponified by means of potassium hydroxide dissolved in methyl alcohol. The acid crystallized from benzene in white needles; these melted at $74-75^{\circ}$ after being dried over sulfuric acid *in vacuo*.

b. Ammonium Salt.—The ammonium salt was prepared from the acid and dilute ammonium hydroxide. It crystallized out as white flakes. Only about 2.9 g. of this salt were soluble in 100 cc. of water at 16° .

c. The silver salt was formed as a white precipitate when the solution of the ammonium salt was treated with silver nitrate solution.

Calc. for $C_{12}H_{22}NO_2Ag$: Ag, 32.53. Found: Ag, 32.19.

d. The copper salt was made by precipitation from the solution of the ammonium salt by means of copper sulfate solution. It was a green, flaky solid when dry.

Calc. for $C_{22}H_{44}N_2O_4Cu \cdot 3H_2O$: Cu, 11.23. Found: Cu, 11.09.

e. The calcium salt was prepared from the acid, water, and powdered calcium carbonate. It came out of solution as white, rhomboidal crystals.

Calc. for $C_{22}H_{44}N_2O_4Ca \cdot 4H_2O$: Ca, 7.14. Found: Ca, 7.18.

f. Diisoamylcyanoacetamide.—The acid chloride was prepared from the acid and phosphorus pentachloride. When it was treated with concentrated ammonia water, the amide was formed. This crystallized from hot alcohol in needles melting at 152° .

Calc. for $C_{12}H_{24}ON_2$: N, 12.50. Found: N, 13.11.

Derivatives of Benzylcyanoacetic Acid.—Benzylcyanoacetic acid was made by the method already described;¹ it was a white, crystalline solid melting at 101° .

a. Lead Salt.—The lead salt was made (1) by addition of a dilute solution of lead nitrate to an aqueous solution of the acid; (2) by addition of the lead nitrate solution to an aqueous solution of the ammonium salt. In each case the lead salt came down as a bulky, white, crystalline precipitate. An analysis of the air-dried salt gave the following figures:

Calc. for $C_{20}H_{18}N_2O_4Pb \cdot 3H_2O$: Pb, 33.97. Found: Pb, 33.83, 33.95.

After the salt had been dried for several hours *in vacuo* over sulfuric acid the figures were:

Calc. for $C_{20}H_{18}N_2O_4Pb$: Pb, 37.30. Found: Pb, 36.87.

The lead salt is soluble in hot water and in hot methyl and ethyl alcohols.

b. Barium and Calcium Salts.—The barium and calcium salts were made from the acid and water, with barium and calcium carbonates, respectively. Both salts were white and crystallized in needles. The anhydrous calcium salt was obtained when its hydrate stood *in vacuo* over sulfuric acid; the other salts were air-dried.

¹ *Am. Chem. J.*, 22, 176 (1899).

Calc. for $C_{20}H_{18}N_2O_4Ca$: Ca, 10.31. Found: 10.42.

Calc. for $C_{20}H_{18}N_2O_4Ca \cdot 3H_2O$: Ca, 9.05. Found: 9.06.

Calc. for $C_{20}H_{18}N_2O_4Ba \cdot 6H_2O$: Ba, 23.10. Found: 23.01.

The barium and calcium salts are soluble in hot alcohol and in hot water.

c. Copper Salt.—The cupric salt was prepared by the addition of a dilute solution of cupric sulfate to the solution of the ammonium salt. It came out as a deep blue precipitate, but turned green when it lost its water of hydration. The water was lost at about 65° ; the salt melted with decomposition and evolution of carbon dioxide at $105-115^\circ$. The percentage of copper was determined by ignition, that of water of hydration by the loss sustained *in vacuo* over sulfuric acid.

Calc. for $C_{20}H_{18}N_2O_4Cu \cdot 5H_2O$: Cu, 12.68. Found: 12.42; H_2O , 17.96. Found: 18.08; N, 5.58. Found: 5.45.

d. Acid Chloride.—The acid chloride of benzylcyanoacetic acid was made from the acid and phosphorus pentachloride. It was a slightly colored liquid that did not distill under 35 mm. when the outside temperature was 290° . When the chloride was treated with an excess of ammonia water it gave benzylcyanoacetamide, melting at 130° .¹

Salts of Dibenzylcyanoacetic Acid.—The acid was made from its ester, boiling at $225-235^\circ$ under 15 mm., and potassium hydroxide dissolved in methyl alcohol. After being recrystallized from benzene it melted at $194-195^\circ$. Cassirer² gives the melting point as $188-189^\circ$.

The silver salt was made from the ammonium salt and silver nitrate. It formed a white precipitate.

Calc. for $C_{17}H_{14}NO_2Ag$: Ag, 29.03. Found: Ag, 29.69.

The copper salt was made from the ammonium salt and cupric sulfate. It came out as a blue precipitate that turned green when dried.

Calc. for $C_{22}H_{22}N_2O_4Cu \cdot H_2O$: Cu, 10.43. Found: Cu, 10.21.

Benzylation of Cyanoacetic Ethyl Ester in Methyl Alcohol Solution: Dibenzylcyanoacetic Methyl Ester.—Twenty grams of cyanoacetic acid ethyl ester were dissolved in 125 cc. of Kahlbaum's anhydrous methyl alcohol and treated with a solution of 4.07 g. of sodium in 125 cc. of methyl alcohol. Benzyl chloride (22.4 g.) was then added and the mixture was allowed to stand for 14 hours. The alcohol was then distilled off and the residue was treated with water and extracted with ether. The ether solution was washed, dried and distilled. The product (19.5 g.) was fractionated under 15 mm. pressure. The fractions were:

I. Boiling up to 101°	5.5 g.	III. $195-250^\circ$	3.2 g.
II. $101-160^\circ$	1.5 g.	IV. $250-260^\circ$	6.7 g.

¹ *Am. Chem. J.*, 22, 180 (1899).

² *Ber.*, 25, 3027 (1892).

Fractions III and IV crystallized when cool. They were dissolved in ether and the ether solution was shaken with 10% sodium hydroxide. The sodium hydroxide solution yielded 1.6 g. of benzylcyanoacetic acid; the ether solution gave 4.9 g. of dibenzylcyanoacetic acid methyl ester, which crystallized when cold. It was recrystallized from an ether-ligroin mixture, coming out as large, six-sided, white plates melting at 78–79°.

Calc. for $C_{16}H_{17}NO_2$: C, 77.43; H, 6.09; N, 5.02. Found: C, 77.81 and 77.69; H, 6.83 and 6.42; N, 5.11.

The methyl ester was also prepared by treatment of the silver salt of dibenzylcyanoacetic acid (*q. v.*) with methyl iodide.

The study of the derivatives of cyanoacetic acid is being continued.

DECATUR, ILL.

[CONTRIBUTION FROM THE HARRIMAN RESEARCH LABORATORY, ROOSEVELT HOSPITAL, NEW YORK.]

A COMPARATIVE STUDY OF AERATION AND HEAT DISTILLATION IN THE KJELDAHL METHOD FOR THE DETERMINATION OF NITROGEN.

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In 1903, Folin¹ described a method for the determination of ammonia in urine based upon its removal by passing a rapid current of air through the solution under suitable conditions, absorbing the ammonia in acid, and titrating the excess of acid.

P. A. Kober,² in 1908, proposed the use of aeration for the separation of ammonia in all Kjeldahl determinations in place of the ordinary heat distillation and described the apparatus and method to be employed. He quoted experiments made by Dr. Kristeller on the estimation of the ammonia in an ammonium chloride solution, three by aeration and two by heat distillation, with excellent agreement.

In the following year, Sebelien³ suggested the same method for all Kjeldahl determinations. He worked with ammonium salts only and studied the conditions necessary for the removal and absorption of the ammonia.

Davis⁴ found aeration to give unsatisfactory results in the determination of nitrogen in cottonseed meal and proposed to heat the solutions during aeration. Gill and Grindley⁵ confirmed the work of Davis with cottonseed-meal, but obtained results agreeing with heat distillation for a number of other substances.

¹ *Z. physiol. Chem.*, 33, 161 (1903).

² *THIS JOURNAL*, 30, 1 (1908).

³ *Chem. Ztg.*, 33, 795 (1909).

⁴ *THIS JOURNAL*, 31, 556 (1909).

⁵ *Ibid.*, 31, 1249 (1909).

In a second paper¹ Kober gave further details for carrying out the method and recorded three results comparing the aeration and heat distillation procedures with magnesium phosphate present, showing practically perfect agreement, while in a third paper² some of the questions involved were discussed further and a number of experiments using the aeration procedure given.

Dillingham,³ following Kober's directions, found with ammonium sulfate that from 3 to 15% of the ammonia remained in the residues after aeration, and that this could be obtained by subsequent heat distillation.

In Kjeldahl determinations made in this laboratory, the aeration procedure has heretofore been used. It was observed recently, in the analysis of certain proteins in this way, that the nitrogen contents were much less than those recorded in the literature. These differences led to a careful study of the factors involved and ultimately to a comparison of the aeration and heat distillation procedures, the results of which are communicated in this paper.

The main point to be emphasized in this study is that in the determination of the ammonia by aeration, not only were the results obtained compared with the theoretical nitrogen contents of pure substances wherever possible and with the results obtained by heat distillation, but every solution which was aerated was then submitted to heat distillation. It may be stated in advance that the results showed the aeration method to be unreliable when compared with the direct heat distillation method.

The conditions stated by Kober to be most suitable were strictly adhered to in carrying out the aeration experiments. The substances given in Table I, dissolved in 20-25 cc. water, were digested with 20 cc. conc. sulfuric acid, 10 g. potassium sulfate, and 0.2 g. crystallized copper sulfate, either for an hour after charring had disappeared or, with urea and uric acid where there was little charring, for an hour after the appearance of dense white fumes. The mixtures were then diluted with 80 cc. of water and 75 cc. of sodium hydroxide⁴ were added with cooling in the aeration apparatus. Aeration was allowed to proceed for two

¹ THIS JOURNAL, 32, 689 (1910).

² *Ibid.*, 35, 1594 (1913).

³ *Ibid.*, 36, 1310 (1914).

⁴ Kober recommended 75 cc. NaOH solution, sp. gr. 1.46-1.48 (48° Bé. obtained in steel drums) for 20 cc. conc. sulfuric acid. He found 52 cc. of this alkali to neutralize 20 cc. of the acid. In the experiments given in Table I, three different solutions of alkali were used. They were made up from sodium hydroxide, electrolytic lumps. Expts. 15, 16, 18, 19, 23, 24, 27, 28, 30, 31, 33, 34, 36, 37, 39, 40 were performed with alkali, sp. gr. 1.461, 46.0 cc. of which were required to neutralize 20 cc. of the conc. sulfuric acid (sp. gr. 1.84 at 13°); Expts. 1, 2, 5, 6, 9, 10, 12, 13, 21, 22, 42, 43, with alkali, sp. gr. 1.444, 49.2 cc. neutralizing 20 cc. of the acid; and Expt. 4, with alkali, sp. gr. 1.401, 55.6 cc. neutralizing 20 cc. of the acid.

hours or some minutes longer and the excess acid then titrated, using alizarin sulfonic acid as indicator. The alkaline mixtures, from the aeration, were then diluted to 300 cc. with distilled water and distilled by heat as in the customary Kjeldahl procedure. Suitable blanks were run frequently in order to eliminate errors which might arise from distilled water, sulfuric acid, etc. A total volume of 400 to 600 liters of air were stated to be sufficient in the aeration for the average amount of ammonia. In order to be certain that these conditions were adhered to, an apparatus was constructed similar to the crude one recommended and the rate of aeration determined immediately before and after each experiment. This ranged from 280 to 390 liters of air per hour for the different experiments. In any one set there was often a difference even up to 30% in testing before and after the run. Taking the mean of the two values in these cases, in general the rate of aeration as measured for the two hours or longer was 330-340 liters per hour.

In the direct heat distillation experiments, the mixtures after digestion were diluted to about 225 cc., 75 cc. of the NaOH solution, sp. gr. 1.444 or 1.461, added, and distilled in the customary way into standard acid.

In Table I are shown the results obtained for a number of nitrogenous substances. Column 1 gives the substance studied, and for simple substances the calculated percentage of nitrogen; Column 2, the number of the experiment; Column 3, the number of cc. of 0.1 *N* acid neutralized by the ammonia driven over in the aeration; Column 4, the number of cc. of 0.1 *N* acid neutralized by the ammonia driven over by heat distillation from the solutions which had just been aerated; Column 5, the number of cc. of 0.1 *N* acid neutralized by the ammonia obtained by heat distillation directly without aeration, that is to say the results as in the ordinary Kjeldahl method; Columns 6-9, the percentages of nitrogen found; Column 6 by the aeration; Column 7 by the heat distillation following aeration; Column 8 the sum of Columns 6 and 7; Column 9 by the direct heat distillation alone. The substances were dried in an electric thermostat at 100-105° to constant weight before analysis. The antitoxin preparations were obtained from Dr. E. J. Banzhaf of the Research Laboratory of the New York Health Department. The castor bean globulin was prepared in the course of an investigation on lipase.

The results given in this table require little comment. For only two substances, the second tetanus antitoxin preparation and tyrosine, are the values found by aeration alone in any way satisfactory. Here the percentage of nitrogen was increased 0.10 to 0.27 by subsequent heat distillation. For the rest of the substances, the nitrogen contents by the aeration procedure were found to be in error (low) by amounts ranging from 0.30 to 1.97%. The sum total of nitrogen found by aeration and subsequent heat distillation agreed very satisfactorily in every case with

TABLE I.—COMPARISON OF AERATION AND HEAT DISTILLATION IN KJELDAHL DETERMINATIONS.

Substance.	Expt. no.	Gram taken.	Cc. 0.1 N acid used.			Percentage nitrogen found.			
			Aera- tion.	Then distn.	Distn. alone.	Aera- tion.	Then distn.	Sum.	Distn. alone.
Casein (Merck)	1	0.1519	15.85	0.52	...	14.62	0.48	15.10	...
	2	0.1530	16.00	0.56	...	14.65	0.51	15.16	...
	3	0.1549	16.72	15.12
Antitoxin preparation (meningitis)	4	0.1496	13.72	0.65	...	12.85	0.61	13.46	...
	5	0.1532	14.29	0.34	...	13.07	0.31	13.38	...
	6	0.1512	14.04	0.37	...	13.01	0.34	13.35	...
	7	0.1518	14.61	13.48
	8	0.1515	14.44	13.35
Antitoxin preparation (tetanus)	9	0.1503	14.16	0.51	...	13.20	0.47	13.67	...
	10	0.1512	14.44	0.32	...	13.38	0.30	13.68	...
	11	0.1510	14.71	13.65
Antitoxin preparation (tetanus)	12	0.1489	14.42	0.26	...	13.56	0.24	13.80	...
	13	0.1511	14.53	0.24	...	13.47	0.23	13.70	...
	14	0.1518	15.01	13.85
Antitoxin preparation (streptococcus)	15	0.1520	14.23	0.36	...	13.12	0.33	13.45	...
	16	0.1507	14.05	0.52	...	13.06	0.50	13.56	...
	17	0.1503	14.60	13.61
Castor-bean preparation (globulin)	18	0.1535	18.04	0.65	...	16.46	0.59	17.05	...
	19	0.1525	18.20	0.41	...	16.75	0.38	17.11	...
	20	0.1517	18.45	17.04
Hexamethylenetetramine (39.99%)	21	0.1016	27.53	1.43	...	37.96	1.97	39.93	...
	22	0.1011	27.93	0.78	...	38.70	1.08	39.78	...
	23	0.1016	28.86	39.79
Uric acid (33.33%)	24	0.1519	35.63	0.45	...	32.86	0.41	33.27	...
	25	0.1512	35.35	0.60	...	32.78	0.56	33.34	...
	26	0.1525	36.25	33.30
Glycylglycine (21.21%)	27	0.1501	22.23	0.58	...	20.75	0.54	21.29	...
	28	0.1517	22.48	0.55	...	20.76	0.51	21.27	...
	29	0.1516	22.92	21.18
Alanyl glycine (19.18%)	30	0.1499	20.12	0.37	...	18.81	0.35	19.16	...
	31	0.1515	20.50	0.33	...	18.91	0.30	19.21	...
	32	0.1518	20.76	19.20
Tyrosine (7.74%)	33	0.2016	10.71	0.39	...	7.44	0.27	7.71	...
	34	0.2018	10.86	0.15	...	7.54	0.10	7.64	...
	35	0.2030	11.09	7.66
Glycine (18.67%)	36	0.1518	19.52	0.69	...	18.02	0.64	18.66	...
	37	0.1513	19.76	0.39	...	18.29	0.36	18.65	...
	38	0.1512	20.10	18.63
Alanine (15.73%)	39	0.1508	16.33	0.55	...	15.17	0.51	15.68	...
	40	0.1525	16.85	0.30	...	15.48	0.28	15.76	...
	41	0.1513	17.00	15.74
Urea (46.66%)	42	0.1028	32.79	1.40	...	44.69	1.91	46.60	...
	43	0.1004	32.24	1.11	...	44.99	1.55	46.54	...
	44	0.1025	34.08	46.58

the nitrogen content found by direct heat distillation in the customary way.

A number of results were obtained with different protein substances in which the heat distillation and aeration methods were used, but in which the solutions after aeration were not heat distilled. The differences ranged for 0.40 to 1.50% in the amounts of nitrogen present, the results by aeration being smaller in every case. As these results add nothing essential to the results given in Table I, they need only be referred to in connection with pointing out the unreliability of the aeration procedure.

Although the scope of this paper does not include the study of the factors upon which the accuracy of the aeration procedure might depend, but only the practical usefulness of the method, some of the results obtained with ammonium sulfate (without digesting) may be of interest and are shown in Table II. The headings of the columns taken in connection with the footnotes and the description of Table I explain the experiments. The rates of aeration are again in the neighborhood of 330 liters per hour and were fairly uniform.

TABLE II.—AERATION AND HEAT DISTILLATION WITH AMMONIUM SULFATE.

Mixture.	Expt. no.	H ₂ SO ₄ cc.	NaOH cc.	Cc. 0.1 N acid used.			Percentage nitrogen found.			
				Aeration.	Then distn.	Distn. alone.	Aeration.	Then distn.	Sum.	Distn. alone.
A	45	..	25	14.17	0.87	...	19.75	1.21	20.96	...
	46	..	35	14.61	0.58	...	20.37	0.81	21.18	...
	47	..	45	14.98	0.19	...	20.89	0.27	21.16	...
	48	..	55	15.15	0.06	...	21.12	0.08	21.20	...
B	49	20	75	14.60	0.48	...	20.35	0.67	21.10	...
	50	20	75	14.83	0.20	...	20.68	0.28	20.96	...
	51	20	75	14.88	0.21	...	20.75	0.29	21.04	...
	52	20	75	14.87	0.18	...	20.73	0.25	20.98	...
	53	20	75	14.81	0.25	...	20.65	0.35	21.00	...
C	54	15.22	21.07
D	55	20	75	14.77	0.36	...	20.67	0.50	21.17	...
	56	15	75	14.82	0.34	...	20.74	0.48	21.22	...
	57	10	75	14.89	0.26	...	20.84	0.36	21.20	...

Mixture A.—Total volume 175 cc. No H₂SO₄ or K₂SO₄, 25 cc. (NH₄)₂SO₄ solution (= 0.1005 g. (NH₄)₂SO₄). Different amounts NaOH solution, sp. gr. 1.444.

Mixture B.—Total volume 175 cc. 20 cc. conc. sulfuric acid, 10 g. K₂SO₄, 0.2 g. CuSO₄·5H₂O, 25 cc. (NH₄)₂SO₄ solution (= 0.1005 g. (NH₄)₂SO₄). NaOH solution, Expts. 49, 50, 51, sp. gr. 1.444; Expts. 52, 53, sp. gr. 1.470.

Mixture C.—0.1012 g. (NH₄)₂SO₄, 20 cc. conc. sulfuric acid, 10 g. K₂SO₄, 0.2 g. CuSO₄·5H₂O.

Mixture D.—Total volume 175 cc. Different amounts sulfuric acid, 10 g. K₂SO₄, 0.2 g. CuSO₄·5H₂O, 25 cc. (NH₄)₂SO₄ solution (= 0.1001 g. (NH₄)₂SO₄). 75 cc. NaOH solution, sp. gr. 1.461.

With Mixture A and different amounts of NaOH solution, practically complete distillation of the ammonia took place with 55 cc. of alkali.

With less alkali, distillation was incomplete, although no acid was present originally in the solution. With Mixture B, the distillation was incomplete with 75 cc. alkali, sp. gr. 1.444 or 1.470, sulfuric acid and potassium sulfate having been added to the solution in amounts corresponding to digestion mixtures. With Mixture D the presence of different quantities of sulfuric acid originally, made only a comparatively small difference in the error of the aeration procedure.

Conclusion.

The aeration procedure in the ordinary Kjeldahl method for nitrogen very often gives inaccurate and therefore unreliable results, and should not be used.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE HARRIMAN RESEARCH LABORATORY, ROOSEVELT HOSPITAL,
NEW YORK.]

STUDIES ON ENZYME ACTION. CORRECTIONS.

By K. GEORGE FALK AND KANEMATSU SUGIURA.

Received January 31, 1916.

In the course of the study of lipolytic actions, some of the results of which were communicated in previous papers, a number of solid preparations were described and analyzed. The nitrogen contents were determined by the Kjeldahl method with the aeration procedure recommended by Kober. The unreliability of this procedure was pointed out in the preceding paper¹ and it is the object of this paper to correct the nitrogen results given in former papers on the basis of the customary heat distillation procedure in the Kjeldahl method.

The esterase preparations from castor beans,² water extract of castor beans, dialyzed, filtered clear, precipitated with acetone, designated E II gave 16.2% nitrogen for the dried material whether dialyzed 5 or 20 hours, while the ash-free material gave 17.0% nitrogen (as against 15.7 and 16.3% by the aeration procedure). The lipase preparations³ L I, saturated NaCl extraction of castor beans residues after water extractions, dialysis, filtration and washing with acetone, gave 16.8% nitrogen for the dried material, and 17.9% for moisture and ash-free material (17.0 by aeration). L II, obtained similarly with 1.5 N NaCl solution, gave 17.1% for moisture-free or 17.9% for ash- and moisture-free material (16.7 by aeration). L II reprecipitated from NaCl solution, gave 18.2% for dried or 18.4% for dried and ash-free substance (17.6% by aeration). The lipase preparation from soy beans,⁴ preparation by water extraction

¹ Cf. also Dillingham, *THIS JOURNAL*, 36, 1310 (1914).

² XII paper, *THIS JOURNAL*, 37, 223 (1915).

³ *Ibid.*, p. 227.

⁴ XIII paper, *THIS JOURNAL*, 37, 651 (1915).

dialysis, filtration, and precipitation by acetone, gave for the dried substance 15.5% nitrogen (14.0 by aeration).

The corrected (higher) nitrogen contents of these substances (especially those obtained from castor beans) approximate more nearly the analyses of similar substances, described by Osborne and others.¹

NEW YORK, N. Y.

[CONTRIBUTION FROM THE BIOCHEMISTRY LABORATORIES OF THE UNIVERSITIES OF ILLINOIS AND SOUTHERN CALIFORNIA.]

NITROGENOUS CONSTITUENTS OF BRAIN LECITHIN.

BY J. E. DARRAH AND C. G. MACARTHUR.

Received February 17, 1916.

The object of the work here reported was to study the hydrolysis products of sheep and beef brain lecithin, with the purpose of determining their nitrogenous constituents, both qualitatively and quantitatively.

Preparation of the Lecithin.—Fresh sheep and beef brain, in separate lots, were finely ground in a food-grinder. They were then allowed to stand in acetone for two days. At the end of this time, the material was filtered, thoroughly pressed in a fruit press, and then put into fresh acetone. The acetone was changed in this way at least three times. The second and third extractions removed most of the fat and some extractives, such as cholesterol. The dehydrated material was kept in a good grade of acetone until it was required for use. Portions of this tissue were filtered out, dried on glass plates in a current of air, and placed in double their volume of benzene. The benzene was agitated in contact with the tissue on a shaking machine. Part of the extractions were made, hot, by allowing a stream of water heated to 65° to flow over the bottle containing the mixture, while it was shaking. The extraction period was from two to four hours. The benzene solution was filtered off and the tissue was freed from benzene so far as possible, by the fruit-press. A second benzene extraction was then made. A few trials were made, using ether instead of benzene extraction. This solvent seemed to be much less satisfactory than benzene, and is more likely to cause oxidation of the lecithin.

The benzene extracts were concentrated almost to dryness, by distilling under reduced pressure, in a carbon dioxide atmosphere, over the steam bath. The light brown residue was dissolved in the smallest possible volume of ether, which had been freshly distilled over calcium chloride. This solution was found to contain cephalin, lecithin, and "white substance." The cephalin was precipitated, by addition of a volume of absolute alcohol equal to two and one-half times the volume of the ether solution. As thus precipitated, the cephalin was a very light brown in color, and in waxy condition, easily pressed together.

¹ Cf. Osborne, "The Vegetable Proteins," 1909.

Any suspended cephalin was filtered out, and the alcohol-ether filtrate was evaporated with diminished pressure in a carbon dioxide atmosphere. The temperature was not allowed to rise above 45° during any distillation period. When evaporated almost to dryness, the residue was dissolved in a small portion of redistilled ether. By addition of a double volume of acetone, the lecithin, together with some "white material" was precipitated. The precipitate was yellow or very light brown, and adhered to the walls of the precipitation jar in waxy masses. After filtering off the ether-acetone solution, the precipitate was thoroughly pressed together with fresh acetone, in much the same manner in which butter is worked to remove the buttermilk.

As rapidly as possible this precipitate was freed from acetone and placed in a vacuum desiccator, over sulfuric acid or calcium chloride. The desiccator was wrapped in cloth to exclude light, and allowed to evacuate for several hours. When thoroughly dry, the material was dissolved in freshly distilled ether and placed in tall, stoppered cylinders. It was allowed to stand in the ether overnight. The "white substance" settled out and the clear supernatant solution was syphoned off. This solution was tested for cephalin, by addition of alcohol. Usually cephalin was present, and the alcohol treatment had to be repeated.

After reprecipitation of the lecithin by the above method, the ether treatment was also repeated, to remove any "white substance" still present. The original benzene extract seemed to contain, in addition to lecithin and cephalin, a protagon which was not completely disintegrated until the alcohol-ether treatment had been repeated several times. It was therefore necessary to repeat the test for cephalin at least three times. As a criterion of purity, the following points were observed: (1) absence of cephalin; (2) no deposition of "white substance," when allowed to stand in ether solution.

In the latter part of the work, the lecithin was precipitated by addition of the ether solution of the material to the acetone, instead of the reverse process. The last purification of the lecithin was made by precipitation with acetone, from a petroleum-ether solution. Six samples of lecithin were prepared, designated as follows:

LECITHIN PREPARATIONS.

Source.	Weight of product. G.
I. Beef brain (old material repurified).....	5.0000
II. Beef brain.....	17.4149
III. Sheep brain.....	4.0620
IV. Sheep brain.....	18.6333
V. Beef brain.....	9.7450
VI. Sheep brain.....	11.5000

Hydrolysis.—The lecithin was hydrolyzed with 3% HCl, or with

1.6–5% KOH in aqueous solution. The hydrolyzing mixture was refluxed for from 15 to 20 hours in an atmosphere of carbon dioxide. After acid hydrolysis, the free fatty acids floated on the surface. In case hydrolysis by KOH had been used, the acids were liberated by acidifying with dilute HCl. The acids were filtered out on a hardened filter, and were washed on the filter with water containing a trace of acid.

Qualitative Study of Nitrogenous Products.

Natural Amino Ethyl Alcohol by Method I.—Lecithin Samples I and II were hydrolyzed with 3% HCl for 15 hours. The filtrates from the fatty acids were combined. The nitrogenous bases remained in the filtrate, together with the glycerophosphoric acid. This solution was evaporated to dryness, using a low temperature. The residue was taken up in the smallest amount of water necessary, and barium chloride solution was added in excess. Ninety-five per cent. alcohol was then added to precipitate the barium glycerophosphate. This precipitate was filtered off, and the filtrate was evaporated to dryness. The residue was taken up in alcohol and evaporated repeatedly, to free it from alcohol-insoluble material. Finally, the residue was taken up once in absolute alcohol and evaporated. It was then dissolved in distilled water. To a volume measuring 120 cc. were added 18 cc. of concentrated HCl, and a solution of 15 g. of phosphotungstic acid dissolved in 30 cc. of water. The solution was made up to 200 cc.; it was warmed slightly, then allowed to cool in the refrigerator.

The choline-phosphotungstate, thus precipitated, was filtered out and washed on the filter with 200 cc. of a solution containing 5 g. of phosphotungstic acid and 6 cc. of concentrated HCl. To the filtrate, phenolphthalein was added, and 50% sodium hydroxide was run in, until alkalinity was reached. The solution was then diluted to 800 cc., and a 20% solution of crystalline barium chloride was added in excess. This removed the excess of phosphotungstic acid. The precipitate was filtered out and washed free from chlorides. Washings and filtrate combined were acidified with HCl, and evaporated to dryness on the steam bath. The residue was extracted with absolute alcohol.

The alcohol solution, thus obtained, was filtered and a warm saturated alcoholic solution of picrolonic acid (1,*p*-nitro phenyl-3-methyl-4-nitro-5-pyrazolon) was added. The picrolonate of amino ethyl alcohol precipitated slowly, after standing in a desiccator, over sulfuric acid or calcium chloride. The crystals had the characteristic appearance, *i. e.*, tufts of yellow needles. After several recrystallizations from alcohol, this derivative was found to soften at 221°, and melted with decomposition at 225°. The salt prepared from synthetic amino ethyl alcohol showed exactly the same crystalline form and melting point. On mixing

the synthetic with the natural derivative, no change in melting point was observed.

Melting point of natural and synthetic, 221–225°.	Wt. sample.	Wt. Ns.	% N.	Theoretical % Ns.
Natural derivative.....	0.1028	0.0218	21.20	21.51
Synthetic derivative.....	0.0743	0.0158	21.26 ¹	...

Synthetic Amino Ethyl Alcohol.—It may be well to outline the procedure followed in the synthesis of the base. The available starting point in the synthesis seemed to be ethylene bromide. A mixture of 175 g. of potassium acetate and 175 g. ethylene bromide with 350 g. of 85% ethyl alcohol were refluxed together for two days on the water bath. The resulting mixture was distilled. The fraction boiling from 130° to 190° was redistilled. Most of it distilled at 182°. This glycol-acetate was saturated with dry HCl gas. The chloracetic ester separated as a brown oil. This oil was placed in a separatory funnel and dropped slowly into a 50% solution of KOH in water. The alkali was warmed slightly at the same time. The resulting vapors were passed through a condenser, cooled by means of ice-water drawn through by the suction of a water pump. The cooled vapors of ethylene oxide were thus conducted into a collecting flask containing a saturated solution of ammonia in ethyl alcohol, and surrounded by a freezing mixture. The flask was provided with a small outlet tube, to release pressure. The alcohol solution, containing the ethylene oxide and ammonia, was allowed to stand tightly stoppered, for two days.

The alcohol solution was fractionated. At first, ammonia vapor and alcohol passed over. Fractions from 85° to 130° were redistilled. Fractions boiling at 120–180° were also redistilled. Finally, combining the higher boiling fractions, all distilled over at 120–140°. This fraction was a light brown oil,² which rapidly grew dark in color. It had a strong basic odor and attacked cork readily. Allowing for small amounts of water and alcohol probably present, the yield was approximately 2 g. The picrolonate derivative of the synthetic base proved to have the same properties as the derivative of the natural base, as previously described. The melting point was 225°. The crystals formed characteristic tufts of yellow needles, with twinning.

Natural Amino Ethyl Alcohol by Method II.—A somewhat different method was used in lecithin Samples III–VI than in Samples I and II, for isolation of the amino ethyl alcohol. Sample III was hydrolyzed with 3% HCl, Samples IV and V with 5% KOH, and Sample VI with 1.6% KOH. Hydrolysis products of Samples III, IV, and V, were com-

¹ This agrees well with Knorr's value, *i. e.*, 21.31% Ns. M. p. 221–225°. *Ber.*, 30, 909 (1897).

² Knorr, *Ber.*, 30, 909 (1897); Wurtz, *Ann.*, 114, 51 (1890); 121, 228 (1862); Atkinson, *Ibid.*, 109, 232 (1859); Simpson, *Ibid.*, 113, 115 (1860).

bined and examined together for amino ethyl alcohol, while Sample VI was treated separately. The solution of chlorides of the base was evaporated to dryness and extracted with absolute alcohol, then a solution of platinum chloride was added to precipitate the choline. The precipitate came down in fine yellow flocks. By recrystallization from dilute alcohol, and ignition of a sample in a porcelain crucible, 31.8% platinum was obtained. The calculated value is 31.64% platinum.¹

The excess platinum was removed from the alcoholic solution of the bases, by saturation with H_2S . The glycerophosphoric acid was not removed as was done in the first preparations, but potassium hydroxide in sticks was added to the strongly concentrated alcoholic solution in a distilling bulb until the solution reacted alkaline. Amino ethyl alcohol was then distilled off, leaving a residue of potassium glycerophosphate. The largest fraction distilled over at 160–165°. The purest fraction distilled at 177–185°. We obtained the same substance (amino ethyl alcohol) as was obtained by the previous method; and with much less trouble. The picrolonate and the chloroaurate were prepared.

The chloroaurate was made by adding concentrated HCl to the base, and then a molecular equivalent of gold chloride in a 3% aqueous solution. After standing a week in a good vacuum desiccator over sulfuric acid, the salt crystallized in needles over a centimeter long, of a golden yellow color. This salt was so hygroscopic that it was difficult to obtain a melting point. After heating in a glass tube immersed in sulfuric acid maintained at 120–150° for two hours, the salt became free from water and melted at 186°. An attempt to crystallize the salt from water solution failed. It was necessary to recrystallize it from concentrated HCl .² Metallic gold separated as the salt crystallized, therefore it was necessary to determine the percentage of gold present as metallic gold, and to deduct this value from the total percentage of gold in the salt. This was done by use of an alundum filter cone.

After treatment with concentrated HCl , washing with water, then with alcohol and ether, the cone was dried in a steam oven. It was then ignited to constant weight. Then a sample of the chloroaurate was weighed out in the cone, treated with concentrated HCl , washed with water, then with alcohol and ether, then dried and ignited as before. The free metallic gold was found to be 2.13%. The total gold was found, by ignition of the chloroaurate, to be 51.31% and 51.52%, in two checks. By subtraction of the metallic gold, 49.18% and 49.39% gold content

¹ Gulewitsch obtained 31.80% platinum. *Z. physiol. Chem.*, 24, 517 (1898).

² Knorr gives 190°.

³ This was also the experience of Trier, *Z. physiol. Chem.*, 86, 153 (1913).

were obtained.¹ The salt obtained by crystallizing the filtrate, from metallic gold in the alundum cone, showed a gold content, after ignition, of 49.40%. Calculated for $C_2H_7NO \cdot HCl \cdot AuCl_4$: gold equals 49.17%.

It seems evident from the boiling point of the free base and analyses of the chloroaurate and picrolonate derivatives, together with a comparison of the same with the synthetic preparations, that one of the nitrogen-containing bases of beef and sheep brain lecithin is amino ethyl alcohol. That choline is also present was confirmed by analysis of the platinum salt, as above described. Sheep and beef brain lecithin, therefore, contain the same nitrogenous constituents as egg lecithin, but in different proportions.

Quantitative Study of Nitrogenous Products.

For some of the quantitative determinations the lecithin used in the qualitative study just described was further purified. It was emulsified in distilled water, enough dilute hydrochloric acid added drop by drop to give a flocculent precipitate. This was rapidly filtered, washed till it began to dissolve, then redissolved in a large volume of water and reprecipitated with hydrochloric acid, washed with water then with acetone. The acetone was removed in a vacuum desiccator. This preparation will be designated *HCl Lecithin*.

The lecithin sample (1, 2 or 3 g., usually 3 g.) was hydrolyzed with 200 cc. of a dilute hydrochloric acid solution (20 cc. HCl + 180 cc. H_2O) for 30 hours. The fatty acids were filtered off and washed three times with dilute hydrochloric acid. A nitrogen determination was run on the fatty acids. This nitrogen is *Residue Nitrogen*.

The filtrate was slowly evaporated to dryness on a water bath to remove the excess of hydrochloric acid and a small amount of fatty acids. The residue was treated with several small portions of water, which were filtered into a 50 cc. measuring flask. The solution was made up to exactly 50 cc. The nitrogen determination on 10 cc. of the filtrate gave *Total Filtrate Nitrogen*.

Another 10 cc. portion was used for the *Amino Nitrogen* by means of amino nitrogen apparatus.² This indicates the amount of amino ethyl alcohol.

Ten cc. were carefully evaporated to dryness, treated with absolute alcohol in several small amounts, filtered, and chloroplatinic acid added in slight excess. The choline platinum chloride was filtered off and a nitrogen determination run on the precipitate. This represented *Choline Nitrogen*.

¹ Knorr's value, % gold equals 49.15% and 49.02%; Trier's value, % gold equals 49.27%.

² Van Slyke, *J. Biol. Chem.*, 12, 275 (1912).

Ammonia Nitrogen was determined on 10 cc. by making it alkaline with 1 g. of potassium carbonate and drawing over the ammonia into standard acid in the usual way.¹

An estimation was made of the *Amino Acid Nitrogen* on the remaining 10 cc. by the copper method.²

The following quantitative data were thus obtained. The figures indicate the percentage of nitrogen in the lecithin.

	Sheep HCl lecithin (new).	Sheep HCl lecithin (new).	Sheep HCl lecithin (5 mo. old).	Sheep lecithin (5 mo. old).	Beef lecithin (new).
Residue nitrogen.....	0.24	0.26	0.31	0.36	0.35
Ammonia nitrogen.....	0.03	0.02	0.05	0.04	0.05
Amino acid nitrogen.....	0.04	0.04	0.05	0.05	0.04
Choline nitrogen.....	0.72	0.75	0.72	0.70	0.53
Amino (alcohol) nitrogen...	0.74	0.72	0.58	0.60	0.75
Total filtrate nitrogen.....	1.55	1.54	1.50	1.38	1.42
Total nitrogen.....	1.79	1.80	1.81	1.74	1.77

Discussion of Quantitative Data.

The residue nitrogen is slightly larger in beef brain lecithin than in sheep brain lecithin. This is undoubtedly due to the fact that the beef brain lecithin available for this work had not been treated with hydrochloric acid and water as had most of the sheep brain samples. Where the latter had not been so treated the amount of residue nitrogen is about the same as in beef brain lecithin. It is not known just what this residue nitrogen represents. However, the study of this fatty acid residue through a separation of the fatty acids by the usual lead acetate method and then a bromination of the unsaturated acids showed that the nitrogen containing part of this residue was with the oleic bromide and could be separated from it by its insolubility in acetone, the oleic bromide being soluble in this reagent. The amount of nitrogen in this acetone-insoluble material was 1.3%. It looks then as though the residue nitrogen represented a substance that has about the same solubilities as the rest of the lecithin that is attached to it either by chemical combination or adsorption so firmly that no known method of purifying the lecithin removes it. That it becomes constant at about 0.25% and that no amount of purification lowers this value lead one to believe it is an integral part of the molecule. Yet it is rather difficult to reconcile this view with the fact that this residue nitrogen substance has the same solubilities it had in the original lecithin even after alkali hydrolysis, the lead acetate separation and bromination. This makes one look upon it as a saturated impurity with properties so similar to lecithin that no known method removes it. Some preliminary experiments on brominating the lecithin

¹ Denis, *J. Biol. Chem.*, 8, 427 (1910).

² Kober, *THIS JOURNAL*, 35, 1546 (1913).

indicate that through the bromo derivative the lecithin can be purified.

The presence of a small amount, almost negligible in most cases, of ammonia is possibly due to a small amount of an ammonium lecithinate, or more probably to a contamination of ammonia from the laboratory during the preparation and hydrolysis, though the usual precautions against contamination were taken. The fact that the amount was so small and so variable supports the latter view.

There is but little amino acid nitrogen in lecithin. This differentiates lecithin from cephalin. The latter has a considerable part of its nitrogen in an amino acid.¹

Choline contains about one-half of the soluble nitrogen of both sheep and beef lecithin. In cephalin, on the other hand, there is no choline.

Most of the other half of the soluble nitrogen is in the amino ethyl alcohol. The amount present is not largely different in sheep and beef brain lecithin, though as a rule there is appreciably more amino alcohol nitrogen and slightly less choline nitrogen in beef brain lecithin. It will be noticed in the analysis that the older samples of sheep lecithin give lower values for amino nitrogen. This would indicate that on oxidation the amino nitrogen slowly changes to some other form.

From this study it can be concluded that sheep and beef brain lecithin contain an unhydrolyzable portion of nitrogen and a hydrolyzable portion, the latter comprising about 85% of the total. Of this soluble portion about one-half of the nitrogen is in choline and the other half in amino ethyl alcohol.

It seems probable that it is merely a coincidence that in brain lecithin the amount of amino ethyl alcohol should approximately equal that of choline. Lecithins from other sources have decidedly different ratios between these two substances. In fact these lecithins are undoubtedly to be distinguished from one another by the varying amounts they contain of these nitrogenous bases. It is even likely that beef and sheep brain lecithin can be differentiated by the higher choline content of the latter.

Conclusion.

(1) The presence of amino ethyl alcohol was demonstrated by analyses of the gold double salt and of the picrolonate derivative. In every respect these analyses were in agreement with the analyses of the corresponding derivatives of synthetic amino ethyl alcohol.

(2) By analysis of the platinum salt, the presence of choline in brain lecithin was confirmed.

(3) These bases (choline and amino ethyl alcohol) were present in both beef and sheep brain lecithin prepared by the above method.

¹ MacArthur, *THIS JOURNAL*, 36, 2397 (1915).

(4) In both sheep and beef brain lecithin the amount of choline nitrogen is about equal to the amino alcohol nitrogen, the two comprising 85% of the total nitrogen in the lecithin.

(5) The other 15% is in the form of an unhydrolyzable residue.

(6) If lecithin is a single substance, and it probably is not, or at least a much more complex one than is usually believed, it probably contains one molecule of each of the nitrogenous bases, choline and amino ethyl alcohol. This associated lecithin molecule is rather firmly combined with a saturated nitrogenous substance which it has been impossible, as yet, to remove.

LOS ANGELES, CAL.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGY OF THE UNIVERSITY OF CHICAGO, THE MEMORIAL INSTITUTE OF INFECTIOUS DISEASES, AND RUSH MEDICAL COLLEGE, CHICAGO.]

THE EFFECTS OF COMMERCIAL GLUCOSE WHEN FED TO WHITE RATS.

By A. J. CARLSON, L. HEKTOEN AND E. R. LECOUNT.

Received February 12, 1916.

In order to study the general effects of commercial glucose when consumed regularly in considerable quantities for a relatively long period of time, young white rats were fed over a period of six months with bread containing a certain amount of glucose. The white rat was selected because it is an easily handled, omnivorous animal whose average span of life covers about three years. For purposes of control another set of rats was fed on bread containing a certain amount of granulated cane sugar and a third set on bread without sugar.

The bread, which was unleavened, consisted of flour, 1000 parts; lard, 25 parts; baking soda, 15 parts; hydrochloric acid, enough to neutralize the soda; water as required for flour, about 655 parts; commercial glucose, 34 parts, in the case of "Glucose Bread," and granulated cane sugar, 26.5 parts, in the case of "Cane Sugar Bread." Fresh lots of the three kinds of bread were baked each Wednesday and Saturday.

In the laboratory in which the experiment took place, white rats are fed on white bread (baker's) about seven days old, small quantities of carrots, and occasionally a little meat. Fresh water is supplied each day. Careful special observations showed that 25 rats of the average weight of 75 g. would eat 275 g. of bread and 170 g. of carrots a day. On the basis of these results and of the general experience, the feeding experiment was conducted with young rats, 25 in each cage, and a daily ration for each cage, to begin with, of 300 g. of bread, 12 g. per rat, 150 g. of carrots or other vegetables, or of meat occasionally, and plenty of

water, all remnants of food being removed and a new supply put in at a certain time each day.

Accordingly, the experiment was started in the early part of April, 1915, with 200 young rats obtained from the Wistar Institute of Anatomy and Biology in Philadelphia during the previous month.

The rats were received in four lots of 50. Lot 1 being born between the first and fourth of February, Lot 2 between the first and eighth, Lot 3 between the first and the tenth, and Lot 4 between the eleventh and eighteenth. The average weight of the animals March 29 varied from 70 g. in the case of the oldest lot to 57.6 g. in the case of the youngest. It should be stated here that in each lot were several rats which were smaller and which grew less than the others ("stunts," "runts").

For the purpose of the experiment each lot was divided into two groups, as nearly as possible of the same weight and proportion as to sex, of 25 each, which were caged separately in galvanized iron cages of the same size and construction; the cages were cleaned regularly and kept in a large well ventilated room in which there were no other animals.

The designation of each group, the kind of bread fed to each group, and the average weight on April 9 are shown in Table I.

TABLE I.

	Designation.	Bread.	Average wt. (grams).	Males.	Females.
Lot 1....	Group 1 A	Glucose	80	11	14
	Group 1 B	Sugar-free	79.2	14	11
Lot 2....	Group 2 A	Glucose	79.1	13	10 (2 "runts" died, one April 5, one April 8)
	Group 2 B	Sugar-free	78	12	13
Lot 3....	Group 3 A	Glucose	68	11	14
	Group 3 C	Cane sugar	75.2	12	13
Lot 4....	Group 4 A	Glucose	60.4	12	13
	Group 4 C	Cane sugar	59.2	13	12

In other words, four groups of 25 rats each were put on glucose bread, two groups on sugar-free bread, and two groups on cane sugar bread. It was thought that this subdivision would offer a good chance for well controlled experiments with different kinds of bread under similar conditions for the different lots as received from Philadelphia.

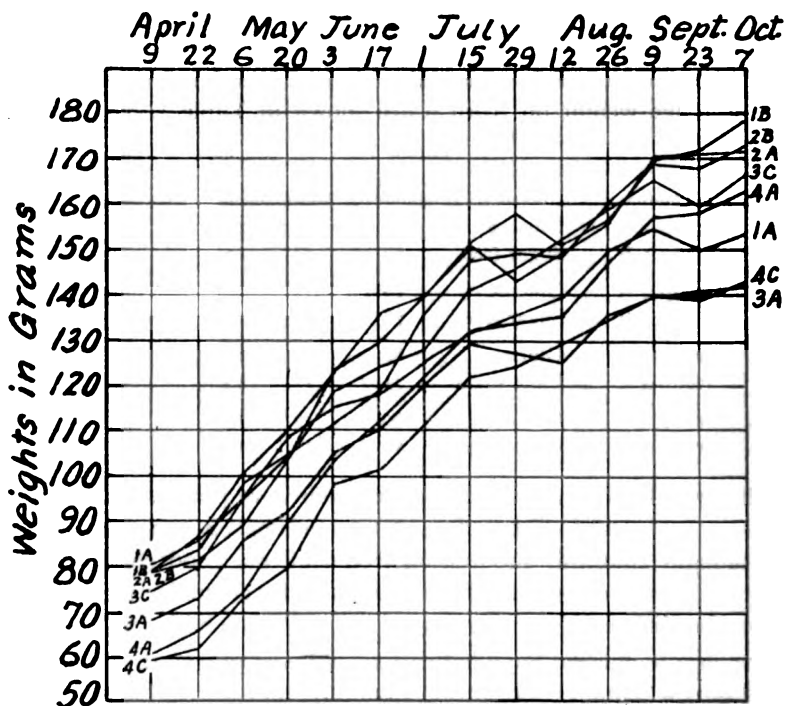
Whenever a female rat gave indications of being pregnant, it was placed by itself on the same ration, proportionately, as before. As soon as the conditions allowed it, such rats were returned each to its group. So far as possible a record was kept of the number of young born in each group. As rats sometimes eat their young and as it may be difficult to detect that a rat is pregnant, this record of the number of young is not absolutely correct.

Sick or untidy rats were isolated in large glass bowls and given a double ration of carrots. They were returned to their group only after complete recovery.

The rats did not escape infections, and during the course of the experiment a number of spontaneous deaths occurred, mostly from pneumonic infection and possibly also from so-called rat typhoid. These infections occurred in all the groups and did not affect the groups fed a certain kind of bread more severely than the other groups.

On May 12 the bread ration was increased to 16 g. per day per rat; on August 23 the carrot ration was increased to 15 g. per rat and day; no other change was made in the food. As a rule the day's supply was wholly consumed at the end of 24 hours with the exception of the hardest of the bread crusts.

The total weight of each group was determined every two weeks and the average weight per rat computed (see Table II and curves). In no



Weight curves of all groups.

case is the weight of young after birth included in the weights. The results show that weight increased at practically the same rate in the various groups.

TABLE II.

Summary of Chief Observations, April 8th to October 7th.

Groups of rats.	April 9.			Died.	Killed.	Approx. number of young.	Young born Sept. 8 to Oct. 7.	October 7.			Increase in wt. %.	Kind of bread fed to each group.
	M.	F.	Av. wt. (g.).					M.	F.	Av. wt. (g.).		
1 A	11	14	80	3	4	43	22	9	9	153.61	92.7	Glucose
1 B	14	10	79.2	6	4	5	3	9	6	178.66	125.5	Sugar-free
2 A	13	10	79.1	5	4	38	18	7	7	171.07	116.2	Glucose
2 B	12	13	78	7	4	30	12	8	6	173.21	122	Sugar-free
3 A	11	14	68	3	4	57	30	7	10	142.16	109	Glucose
3 C	12	13	75.2	7	3	22	7	9	6	166.66	121.6	Cane sugar
4 A	12	13	60.4	5	4	53	15	10	6	163.12	170	Glucose
4 C	13	12	59.2	6	4	54	32	6	9	143.33	142	Cane sugar

Whenever possible, gross and microscopic examination was made of all rats that died spontaneously. On July 13 and again on August 23 two rats in each group, the subjects of the experiments on antibody production detailed on p. 7, were killed and the organs examined. At the conclusion of the main experiment all the surviving animals were killed and examined. The results of the gross and microscopic examination did not differ in the case of any group from those in the other groups and no changes attributable to diet were found. Practically all deviations from the normal standards resulted from infection and involved mostly the lungs.

Experiments on Antibody Production.

In order to test the power of the rats fed on glucose bread, as compared with those fed on the other kinds of bread, to produce antibodies, two special experiments were made. The particular antibody studied in this case is the antibody against the red corpuscles of the sheep. The reason for using the antibody against sheep corpuscles for this experiment was that its course and amount in the rat are known from previous work, thus providing a basis for comparison.

As stated two experiments of this kind were made; namely, on July 7 and August 16. On each occasion two rats from each group were injected in the abdominal cavity with 5 cc. of a 10% suspension of sheep blood per kilo of weight of rat. These rats were killed 6 days later and the amount of the antibody in question determined in the usual way. One injected rat Group 3C died of pneumonia August 22.

The results are shown in Table III; the figures give the highest dilution of the blood serum of the rats in which the action of the antibody against sheep corpuscles could be detected.

The table shows that the rats fed on glucose bread and the rats fed on the other kinds of bread produced about the same amounts of antibody, and these amounts correspond very well to the amount ordinarily

produced by rats injected the same way but living under the usual laboratory conditions.¹

TABLE III.—SHOWING AMOUNT OF ANTIBODY TO SHEEP CORPUSCLES IN RATS INJECTED WITH SHEEP BLOOD.

Groups.	Highest active dilution of rat serum.				Kind of bread fed to each group.
	Rats injected July 6. Tested July 13.		Rats injected Aug. 16. Tested Aug. 23.		
"1A"	24567	24567	12288	12288	Glucose
1B	6144	12288	12288	12288	Sugar-free
2A	1536	24567	12288	6144	Glucose
2B	24567	12288	12288	24567	Sugar-free
3A	24567	12288	24567	24567	Glucose
3C	12288	12288	1	12288	Cane sugar
4A	12288	12288	3072	12288	Glucose
4C	6144	24567	6144	12288	Cane sugar

The results indicate that the power to produce antibodies is not diminished in rats fed as in this experiment, and permits the inference that glucose as here given does not reduce the resistance to infection.

Discussion of the Results.

The summary of the principal observations shows that the number of deaths from infections are about the same in the glucose fed and the control groups.

The percentage increase in the body weight is for the groups fed on glucose bread 122%; on plain bread, 123.5%; on cane sugar bread, 131.8%. For some reason the number of young born in the glucose fed groups was larger than in the other groups and this fact probably accounts for the slightly lower rate of growth in the former.

The value of commercial glucose as food depends (1) on the extent to which the *d*-glucose and the dextrans are absorbed from the digestive tract and oxidized in the body; (2) on the absence of deleterious by-products or contaminations in the glucose; and (3) on its palatability.

Our experiments do not show to what extent the glucose is absorbed and oxidized, as the rats were given as much food as they would eat, and this was probably more than the minimum required for growth and maintenance. Recently Sansom and Woodyatt³ have shown that in dogs with phlorhizin glucosuria the percentage of commercial glucose (*per os*) appearing as blood sugar is but slightly less than on feeding equal amounts of pure dextrose. The physiological literature gives no support to the view that the products of acid hydrolysis of starch are essentially

¹ See Hektoen, "The Formation of Antibodies in Rats Fed on Pure Vegetable Proteins" (Osborne-Mendel Stunting Food), *J. Infect. Dis.*, 15, 279 (1914).

² Died of pneumonia.

³ *J. Biol. Chem.*, 24, 13 (1916).

different from the products of enzyme hydrolysis of starch. In the absence of definite experiments to the contrary one is therefore justified in concluding that the greater part of the dextrans and the dextrose in commercial glucose are utilized in the carbohydrate metabolism of the body.

In regard to the question of deleterious by-products and contaminations our experiments seem conclusive. There is practically no difference in the rate of growth, in resistance to infection, and in immune reaction in the glucose fed and the control rats. Postmortem examination revealed no lesion that could be traced to the diet in any of the groups. It should be pointed out, in this connection, that the quantity of glucose consumed per day by each rat was really considerable, namely, 2.5 g. to 3.5 g. per kilo body-weight, covering a period of about one-sixth of the total span of life of the rat. A parallel test on a group of persons weighing each 60 kilos and living sixty years on the average would mean a daily consumption of 150-200 g. commercial glucose per day for 10 years.

When the processes of manufacture are properly safeguarded deleterious admixtures in glucose from impurities in the chemicals employed are excluded. The sole remaining source of possible injurious by-products appear to be the acid hydrolysis of minute trace of proteins retained with the starch. However, there is no evidence that traces of such hydrolyzed proteins would be injurious when fed by mouth. On the contrary, it is well known that the products of acid hydrolysis of proteins are utilized in the protein metabolism of the body, even to the degree of maintenance of nitrogen equilibrium under certain conditions.

TABLE IV.—TABLE OF AVERAGE WEIGHTS.

Date.	1 A.	1 B.	2 A.	2 B.	3 A.	3 C.	4 A.	4 C.
April 9.....	80	79.2	79.1	78	68	75.2	60.4	59.2
April 22.....	86.28	84.2	86.52	82.3	73.2	79.6	66	62.4
May 6.....	95.6	97.83	100.87	89	86	95.8	74.17	73
May 20.....	108	105	110	104.73	92	104.8	89.83	79.85
June 3.....	115.6	110.86	123	123.15	105	119.79	104.34	98.12
June 17.....	117.56	118	136	129.42	110	124.16	112.6	101.73
July 1.....	126.4	135.78	139.47	138.94	120.8	127.91	121.95	110.86
July 15.....	131.76	147.05	150.47	151.88	129.13	141.52	133.09	122.1
July 29.....	135	148.88	143.33	157	127.4	145.75	134	124
Aug. 12.....	139.5	147.64	148.23	150.58	125.9	151.66	135.5	129.16
Aug. 26.....	149.44	160	156.33	156.66	134.47	158.75	147.77	135
Sept. 9.....	154.88	169.33	170	168.57	138.68	165.62	156.76	139.37
Sept. 23.....	150	172.06	170.71	167.85	140.05	159.62	158.23	138.66
Oct. 7.....	153.61	178.66	171.07	173.21	142.16	166.66	163.12	143.33

The palatability of a food is a factor in its food value in relation to appetite and appetite secretion of gastric juice. In the case of sugar

mixtures or syrups, palatability is essentially a question of degree of sweetness and character of flavor. It is well known that in equal concentrations *d*-glucose does not taste as sweet as cane sugar. However, the degree of sweetness and the character of the flavor preferred in a given food varies with the individual. The factor of palatability does not enter in the use of glucose in bakery products and confections, where the taste and flavor are determined by other ingredients.

Summary and Conclusions.

The addition of commercial glucose in the amounts of about 2.5 g. to 3.5 g. per kilo body weight per day to the diet of white rats for a period of six months has no abnormal influence on the animals, either favorable or unfavorable, as determined by the rate of growth fecundity, immunity reactions, and the condition of the organs.

As both the glucose fed and the control groups of rats were kept on a liberal diet throughout the observation period, the experiment does not show to what extent the commercial glucose was actually absorbed and oxidized, but in the quantities fed the commercial glucose certainly has no injurious effects.

CHICAGO, ILL.

[CONTRIBUTION FROM NORTHWESTERN UNIVERSITY MEDICAL SCHOOL.]

A SIMPLE CELL FOR THE DETERMINATION OF HYDROGEN ION CONCENTRATION.

By J. H. LONG.

Received February 28, 1916.

Since the importance of the determination of H ion concentration has been recognized in so many fields of research there has been no end of suggestions as to types of cells assumed to have distinct advantages for the purpose in this or that direction. While, theoretically at least, the use of two hydrogen electrodes, the electrode in the liquid under investigation balanced against the similar electrode in a liquid of known ion concentration, is logically the simplest and most direct arrangement for the observation in hand, most attention has recently been given to the combination made up of one hydrogen electrode in the liquid plus a known calomel electrode. The advantage in this case is found mainly in the fact that the experiment requires the preparation of only one side of the cell, the calomel electrode being constant. In practical work, therefore, the double hydrogen electrode scheme has been largely abandoned, especially in physiological researches.

In cells constructed in part of the calomel electrode the recent types involve the recognition of the principles brought out in the researches of

Soerensen,¹ Hasselbalch² and others, in which the great advantage of a thorough agitation of the liquid and the overlying hydrogen is made plain. The constancy of potential is soon reached in this way, which is a matter of importance where many tests are being made. The Hasselbalch cell itself³ is excellent, but it is somewhat fragile and the large number of ground glass stopcocks make it relatively expensive at the present time. Among several suggested improvements the cell described recently by Clark⁴ seems to satisfy fully all requirements for accuracy and convenience in manipulation. A constant potential is soon reached with it.

In this laboratory we have experimented with several forms of home-made cells which can be put together with materials at hand without complicated glass blowing or expensive stopcocks, and have found that with some very simple arrangements it is possible to secure a considerable degree of accuracy. Such tubes as are described by Michaelis and Rona⁵ are of this category. Speed and convenience in use may be lacking in such forms, however. The Clark apparatus leaves little to be desired in these respects, but its relatively complex construction makes it rather expensive, especially where but few determinations are to be made. This limits its usefulness. In many lines of investigation the great accuracy which may be reached with this and some other forms is not really necessary, in view of the uncertain character of much of the material to be tested. A satisfactory result with less costly apparatus may be desirable.

A simple form of cell which has been used for some work in this laboratory is shown in the figure. It holds about 15 cc. of liquid, but the amount present during the test is about one-third of this, the rest of the space being occupied by the hydrogen. The cell is essentially a large Y tube, with one branch quite narrow. The liquid is admitted at A in the smaller figure and flows out at B. The wide branches of the Y are closed by small rubber stoppers with two holes, the exposed surfaces being covered with melted paraffin. This coating is perfectly satisfactory and can be renewed when the cell is cleaned. Through one of the holes of one of the stoppers a small, glass tube, filled with mercury, passes and this connects with the platinized electrode by means of a platinum wire. The washed hydrogen passes through from D to C, which are very narrow tubes. Small, rubber tubes over these may be closed by pinchcocks, by means

¹ Soerensen, *Biochem. Z.*, 21, 131 (1909); also *Ergebnisse der Physiologie*, 12, 393 (1912).

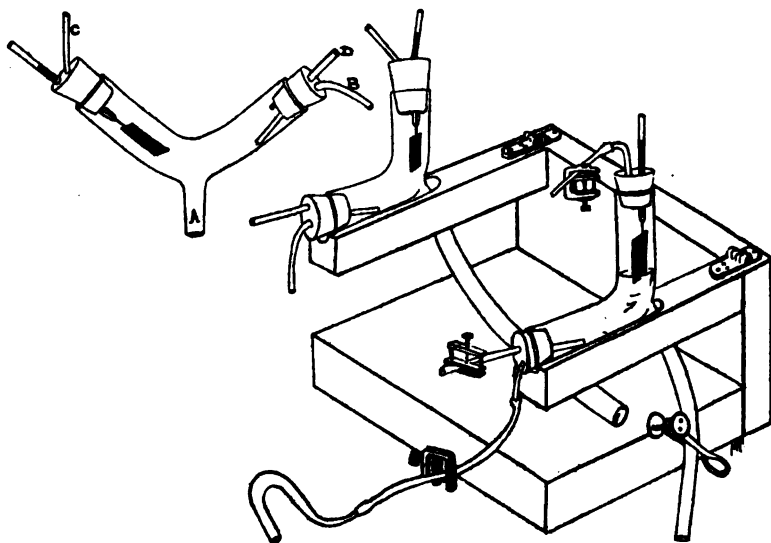
² Hasselbalch, *Biochem. Z.*, 30, 317 (1911); 49, 451 (1913).

³ *Loc. cit.*, 30, 317 (1911).

⁴ *J. Biol. Chem.*, 23, 475 (1915).

⁵ *Biochem. Z.*, 18, 317 (1909).

of which the flow of the hydrogen may be regulated. The liquid exit tube is connected by means of a capillary tube, extended into a much wider tube, with the bridge intermediary vessel containing 3.5 *N* KCl and connected in turn with the calomel electrode.



At the right of the figure is shown a pair of such cells mounted in the position for use. They rest on short wooden arms to which they are fastened by rubber bands. These arms are hinged to a strong support which gives stability to the apparatus. By means of the hinge it is possible to incline the arm at any angle and thus regulate the depth to which the platinum is immersed in the liquid. The hydrogen is distributed in the two branches without breaking the liquid connection. The hinge arrangement provides also for the rapid agitation of the liquid and gas mixture. This requires no additional mechanism; raising and dropping the bar by the finger is sufficient.

The apparatus has been tested in comparison with Hasselbalch cells and by the use of liquids of known hydrogen ion concentration. The final results are the same where an accuracy of about 0.5 millivolt is sufficient, and in the readings both the capillary electrometer and a delicate galvanometer have been used. Constant readings are secured in about ten minutes after filling with liquid and hydrogen and agitating. For example, an observation with a mixture of equal volumes of Soerensen's primary and secondary phosphates at 20° gave a π value of 0.7341, from which,

$$P_H = \frac{0.7341 - 0.3379}{0.0582} = 6.808.$$

A normal urine tested at 21° at short intervals gave the following readings after finishing the shaking at 2 hours and 15 minutes:

Readings at.....	2:30	2:34	2:40	2:45	3:07	3:16	3:55
π	=0.5988	0.6476	0.6468	0.6475	0.6476	0.6476	0.6479

Constant potential values appear in about ten minutes. Slight compression of the pinchcock on the tube leading to the potassium chloride bridge has about the same effect as closing the glass stopcock in the other forms of apparatus. It is of advantage to insert a plug of washed cotton in the bent tube leading to the potassium chloride.

CHICAGO, ILL.

NEW BOOKS.

Elementos de Fisica Geral (Elements of General Physics). By F. J. SOUSA GOMES, Professor in the Faculty of Science in the University of Coimbra, and ALVARA R. MACHADO, Assistant Professor of Physics in the University of Porto. Livraria, Escolar de Cruz & Cie, Braga, Brazil.

As the title page states, this book of some 260 pages is "For use in the Portuguese Lyceums (6th and 7th grades), Gymnasias, and Normal Schools of Brazil."

It is the first part of a larger work, subsequent parts of which will presumably deal with the subjects of heat light, magnetism and electricity.

It differs from most similar works of American origin in the sequence of the arrangement of the subject matter, the order being:

(1) Generalities (28 pages), (2) Mechanics (91 pages), Gravity, not treated under Mechanics, but separately (40 pages), and (4) Properties of matter (100 pages).

The type is excellent as are the cuts, of which a liberal use is made. The treatment of the subjects discussed is distinctly mathematical. It is a book which is calculated to give a diligent student a good grasp of the fundamental laws and phenomena of the branches of physics which it embraces.

W. N. BERKELEY.

Quantitative Laws in Biological Chemistry. By SVANTE ARRHENIUS. London: G. Bell & Sons. 1915. Pp. vii + 173.

This interesting and stimulating book should be in the hands of every biologist, biological chemist and pathologist. It treats of many complex and obscure phenomena of biochemistry in a simple and illuminating fashion, showing how they are to be explained. Arrhenius, as is well known, has emphasized for some time the importance of physical chemistry conceptions in the elucidation of biochemical reactions, and he has made many contributions of value illustrating his point of view. A series of

lectures given before the Royal Institution in 1914 has been expanded into this book. He treats very simply of the method of representing graphically quantitative results, and how to interpret the curves. These general remarks are illustrated by many examples in biochemistry, such as the velocity of coagulation of egg-white and hemoglobin, the temperature coefficient of many vital processes, the rate of destruction of various lysins, toxins and antitoxins by heat and the body, the rate of killing of bacteria by antiseptics. He even shows how perfectly the absorption of food from the intestine can be quantitatively represented by a very simple expression. Schütz's rule and the laws of enzyme action are given a rather extensive treatment. But by far the most illuminating and delightful part of the book are the chapters on chemical equilibria and immunity. The complex facts of immunity are represented with a simplicity of statement as remarkable as it is rare, the uselessness of the complex explanations of Ehrlich and his school pointed out, and the processes brought into relation with very simple chemical reactions.

There is no doubt that this book, together with the biological portion of the *Tables Annuelles Internationales de Constantes et Données Numériques* mark the beginnings of a new era of precision and clarification greatly needed by all the biological sciences. It is, therefore, exceedingly welcome.

ALBERT P. MATHEWS.

Representative Procedures in Quantitative Chemical Analysis. By FRANK AUSTIN GOOCH. viii + 250 pages, 35 figures. John Wiley & Sons, Inc. Price, \$2.00.

One would expect from the pen of Gooch a distinctive work on quantitative chemical analysis and the expectation is amply realized in the present volume. A sentence in the preface states exactly the manner in which the subject matter is handled: "Procedures have been discussed in relation to their essential features, underlying principles and varied applications."

Throughout the book the procedure, that is, the chemistry of the precipitations, titrations, etc., is emphasized rather than physico-chemical theories or special applications. Everything is subordinated to these general discussions. The laboratory exercises are even printed in small type and written in a colloquial style as if to indicate that the main idea should be to understand general applications rather than to carry out a certain volume of laboratory work.

The strongest sections are the ones on general gravimetric and volumetric analysis. In the latter, iodometric processes are given special attention. In the treatment of normal solutions it is pleasing to note that the old and cumbersome available oxygen idea has been dropped in the description of oxidizing and reducing solutions and one depending upon the valence changes involved in the reaction introduced.

In the pages devoted to physico-chemical theory the familiar term solubility product is missing. The reviewer does not know whether to criticize this or not. The case is less doubtful on Page 31, where the old Ostwald calibrating pipette with its rubber tubes and pinchcocks is illustrated and the Morse and Blalock apparatus referred to in the footnote. A reversal of this would have been in the interests of accurate measurement.

It is possible that the subordination of laboratory exercises to general principles will make the book more difficult to use in teaching, especially with large classes, but this after all will depend upon the instructor and the reviewer wishes his last word to be, that Professor Gooch has produced a notable work on quantitative analysis and one to be recommended to every serious student of the subject. C. W. FOULK.

Manual of Quantitative Chemical Analysis. By J. O. FRANK and E. A. CLEMENS xii + 123 pp. Second Edition. Chicago and New York: Row, Peterson & Co. Price, 80 cents.

The first edition of this little book was reviewed in the January, 1915, number of THIS JOURNAL and it is a pleasure to note that there is great improvement in the second edition. The printer and binder have done their parts much better and the authors have also eliminated some of the errors that slipped by them before. It is a pity, however, that the English was not thoroughly revised, for the pages are still full of laboratory colloquialisms. C. W. FOULK.

Food Analysis, Typical Methods and the Interpretation of Results. By A. G. WOODMAN, Associate Professor of Food Analysis, Massachusetts Institute of Technology. McGraw-Hill Book Co., New York, 1915. Small octavo, x + 510 pp. Price, \$3.00.

The following condensed outline of the contents of the book will indicate the sequence of topics and the assignment of space: General methods (specific gravity, index of refraction, moisture, ash, colorimetric determinations, extraction methods, determination of nitrogen, centrifugal methods), 30 pages; Microscopical examination of foods, 21 pages; Food colors, 35 pages; Preservatives, 19 pages; Milk and Cream, 41 pages; Edible fats and oils, 81 pages; Carbohydrate foods, 73 pages; Cocoa and chocolate, 31 pages; Spices, 31 pages; Vinegar, 16 pages; Flavoring extracts, 35 pages; Alcoholic liquors, 81 pages; Photomicrographs, 8 pages; Index, 8 pages.

It would seem that a general chapter on proteins (corresponding to those on carbohydrates and fats) should be included.

Within the limitations which the author has set for himself the book leaves little to be desired. As was to be expected in the work of one so favorably known as a teacher and expert in food analysis, the descrip-

tions of methods and discussions of results are clear, concise, authoritative and modern.

The purpose of the author, as explained in his preface, is to provide a book primarily suited to the needs of the undergraduate student of analytical chemistry, more concise than Leach's Food Analysis and affording more explanation and discussion than the bulletin of methods of the Association of Official Agricultural Chemists. The ground covered is amply sufficient to occupy the time that can usually be devoted to food analysis in a college course. Special attention is given to the suitability and limitations of methods and the interpretation of the analytical results. The author holds that the principal asset to be gained by the student from any detailed consideration of the methods employed to detect adulteration in foods, is the exercise of judgment and the training of the sense of discrimination derived from a critical balancing of the data obtained in an analysis against the natural variations in composition, to determine whether or not they imply artificial manipulation of the product. So consistently does the author adhere to this point of view that he professedly selects foods for discussion according as they illustrate methods of detecting adulteration and without reference to their importance either industrially or to the consumer. This will seem unfortunate to those who believe that students of food chemistry should not merely be trained to do the police work of detecting adulterations but should be equally prepared for more constructive service, whether in the employ of the food industries or of the consuming public.

Among teachers whose courses in food analysis are essentially devoted to the detection of adulterations and who desire a text-book of the character of the well-known work of Leach, but of size suitable for the use of undergraduate students, the present volume is sure of a cordial welcome. It will also be useful to professional chemists because of its convenient conciseness, its recognition of recent developments including those recorded in the foreign literature, its occasional citations of data from "Notices of Judgment" giving the analytical evidence on which successful prosecutions have been instituted under the Food and Drugs Act, and especially because of the incorporation of the experience of Professor Woodman's own laboratory as illustrated conspicuously in the section devoted to the detection of artificial colors in foods. H. C. SHERMAN.

Feeds and Feeding. A Handbook for the Student and the Stockman. By W. H. HENRY, D.Sc., D.AGR., Emeritus Professor of Agriculture, University of Wisconsin, and F. B. MORRISON, B.S., Assistant Professor of Animal Husbandry, University of Wisconsin. Fifteenth edition, revised and entirely rewritten. One volume of 691 pages, octavo. Madison, Wisconsin: The Henry-Morrison Company. Cloth, \$2.25.

This book, which was originally published in 1898, has received wide-

spread favor by practical stockmen and students of animal husbandry. This last revision includes the results of the most recent published and unpublished data of our experiment stations on the science and practices of livestock feeding. The book has been enlarged by the addition of 85 pages.

In Part I the fundamental principles of animal nutrition are first briefly presented, including the most recent discoveries in biological chemistry. The various feeding standards for the different classes of farm animals are fully discussed. To point out some of the more economical points which should be considered in the feeding of livestock, a new chapter—Economy in feeding livestock—has been added.

In Part II many new feedingstuffs are given full consideration along with the old, especial emphasis being placed upon the importance of combining the legume roughages with corn and other cereals for the economical feeding of farm animals and upon the great value of silage for the various classes of livestock. The vital relation of animal husbandry to the economical maintenance of soil fertility through the return to the soil of the manurial residue of feedingstuffs is emphasized.

In Part III there is presented the most important findings so far obtained by the experiment stations on the value of the different feedingstuffs for each class of livestock and on the effect of various methods of preparing feed, systems of feeding and care of livestock, etc.

This revised edition of *Feeds and Feeding* is even more valuable than the previous editions. It presents a large amount of fundamental information as to feeds and feeding in a clear, instructive and readable form. The revised tables in the appendix giving the average percentage composition of American feedingstuffs, the average digestibility of American feedingstuffs, and the digestible nutrients and fertilizing constituents in American feedingstuffs are valuable for general reference work.

H. S. GRINDLEY.

The Physiology of the Amino Acids. By FRANK P. UNDERHILL, PH.D., Professor of Physiological Chemistry, Yale University. One volume of 169 pages, crown octavo, illustrated by cuts, tables and diagrams. New Haven: Yale University Press, 1915. Cloth, \$1.35.

Professor Underhill presents in this little book a clear, accurate and very readable account of the recent fundamental and important discoveries relating to the role of amino acids of proteins in the nutrition of the animal body. In this volume he presents the only compilation available at present of the results of the recent developments in the biochemistry of the amino acids. The nature of the contents of this book is evident from the following titles of the several chapters: The proteins and their derivatives, the amino acids; digestion and bacterial activity in relation

to the amino acids; the absorption of proteins and amino acids; in what form does ingested protein enter the circulation? theories of protein metabolism; the further fate of amino acids; the amino acids in relation to the special dynamic action of proteins; the amino acids and simpler nitrogenous compounds as foodstuffs; and the specific role of amino acids in nutrition and growth. A complete index is given. At the end of each chapter references are given in which all the important literature upon the topic considered is cited. Every chemist, biologist and every student in these fields of study should read this delightful little book.

H. S. GRINDLEY.

Soil Conditions and Plant Growth. By EDWARD J. RUSSELL. Pp. viii + 190. New edition. New York: Longmans, Green and Company. 1915. Price, \$1.50 net.

The purpose of the author is "to give a concise account of our present knowledge of the soil as a medium for plant life," keeping in view "a critical examination of the foundations of our beliefs." The plan and scope of the book are indicated by the following chapter headings: (I) Historical and introductory; (II) The requirements of plants; (III) The constitution of the soil; (IV) The carbon and nitrogen cycles in the soil; (V) The biological conditions of the soil; (VI) The relationship between the microörganic population of the soil and the growth of plants; (VII) The soil in relation to plant growth; (VIII) Soil analysis and its interpretation.

In these days of personal bias and short perspective on the part of some workers in this field, the author shows admirable breadth of view, openness of mind and clear judgment. While every chapter is thoroughly interesting, Chapters V and VI are especially so. The book is a real addition to the literature of the subject.

L. L. VAN SLYKE.

An Introduction to the Principles of Physical Chemistry, from the Standpoint of Modern Atomistics and Thermodynamics. By EDWARD W. WASHBURN, Professor of Physical Chemistry in the University of Illinois. McGraw-Hill Book Company, New York, 1915. Pp. xxv, 445. Price, \$3.50.

The preface gives a better idea of this interesting and valuable book than the title, for the treatment is by no means elementary in nature, and, as the author says, "Many portions of the book can scarcely be pursued to advantage by most beginners in the subject, except under the direction of a competent instructor." The book deals with the theoretical and not with the laboratory side of physical chemistry, and wisely makes use of the calculus without apology. To quote again from the preface: "Perhaps the most radical departure from the custom which under the leadership of Ostwald has prevailed heretofore in most textbooks of Physical Chemistry is in connection with the manner in which atomistics and molecular kinetics are treated. Instead of considering

these systems in a special chapter as interesting but unnecessary hypothetical explanations of observed facts, they are themselves in their most essential features treated as facts already established beyond the possibility of reasonable doubt, and together with thermodynamics, are made to serve as the framework for the development of the whole subject."

It is interesting thus to see the pendulum of thought swinging violently backwards and forwards within a generation. Twenty years ago, to many chosen spirits the atomic theory was anathema; here it is welcomed and even maintained as certain reality. The reviewer cannot help feeling that the position of equilibrium, although nearer the later than the earlier extreme, lies somewhere between the swings. Is there not a real distinction between "facts" perceived by the senses, and interpretations (however useful and vivid) conceived by thought and fancy?

Whatever opinion one may form upon this subject, everyone must agree that the book under discussion shows wide knowledge of Physical Chemistry (especially of the most recent developments) and scholarly thermodynamic treatment of its most important aspects. Even the beginner will be stimulated by some of the chapters; every advanced student of Physical Chemistry will find the book valuable and interesting; and every teacher of this subject will welcome it as a new and efficient aid in helping others over some of the harder parts of the way.

THEODORE W. RICHARDS.

Boden-Bakterien und Boden-Fruchtbarkeit. By DR. F. LÖHNIS. Published by Gebrüder Bornträger, Berlin, 1914. 70 pp. + vi. Price, M. 1.20.

This little volume contains a very illuminating discussion of soil bacteria as a factor in soil fertility. In writing the treatise the author was evidently guided by the wish to bring to the attention of the progressive farmer the more important developments in soil biology. Accordingly he points out in the preface that the average land owner, though he may be averse to reading massive treatises, should interest himself in soil bacteriological problems for they bear a direct relation to the productiveness of his fields.

A portion of the book is devoted to a rather compact review of the more striking facts in the history of soil biology from the time of Schwann and Ehrenberg down to our own day. Mention is made among other matters of the very suggestive pamphlet by Kette, published in 1862, and entitled "Die Fermentations-Theorie gegenüber der Humus—Mineral und Stickstoff-Theorie." The author also takes occasion to mention that soil bacteriology owes a real debt to practical landowners like Kette, von Rosenberg-Lipinsky, Schultz-Lupitz, Caron and Arndt.

The following paragraphs are given over to a consideration of the im-

portant factors of soil fertility including the reserves of mineral and organic plant-food constituents, the nature and functions of "humus," the gains and losses of soil nitrogen; the biological activities which affect the supply of available nitrogen compounds to crops, the transformation of the so-called mineral constituents of plant food as affected by the activities of microorganisms and the utilization of our knowledge of soil microorganisms in providing economically a more abundant supply of nitrogen to cultivated plants.

JACOB G. LIPMAN.

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THE DETERMINATION OF CARBONIC ACID, COMBINED AND FREE, IN SOLUTION, PARTICULARLY IN NATURAL WATERS.¹

BY JOHN JOHNSTON.

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Owing to the importance, especially in connection with water analysis, of a knowledge of the concentration of carbonic acid, combined and free, in solutions, a great deal of attention has been devoted to methods of de-

¹ A few days after this paper was originally submitted to the editor, Professor H. N. McCoy transmitted to me two manuscripts sent to him by Mr. C. A. Seyler (of Swansea, England) entitled: "Studies of the Carbonates. II. Hydrolysis of Sodium Carbonate and Bicarbonate, and the Ionization Constants of Carbonic Acid," by C. A. Seyler and P. V. Lloyd, and "Studies of the Carbonates. III. Lithium, Calcium, and Magnesium Carbonates," by C. A. Seyler. After reading these papers I decided to recall my paper, and to delay its publication until I should have corresponded with Mr. Seyler, who has very courteously allowed me to make use of his MSS. I have changed my calculations in order to have them consistent with this most recent determination of the constants; but the resulting slight changes in numerical values have in no wise affected the general argument of the paper. Quite recently Mr. Seyler has forwarded to me a manuscript copy of a third paper "Studies of the Carbonates. IV. The Hydrolysis of Sodium Bicarbonate and the Ionization Constants of Phenolphthalein," in which the suitability of phenolphthalein as an indicator for the titration of carbonates and carbonic acid is discussed in detail. These three papers will, it is expected, be published in the near future in *J. Chem. Soc.*

termination of these constituents; but the question as a whole has hitherto received scant attention, in particular from the theoretical standpoint. It is the purpose of the present paper to discuss the methods of estimating carbonic acid and carbonate from the point of view that the several molecular species with which we are here concerned can co-exist only in definite proportions determined by the known equilibrium constants, and by this means be enabled to judge of the applicability and degree of accuracy of the several methods. This treatment on the basis of fundamental principles enables us, as we shall see, to criticize and coördinate the numerous apparently contradictory statements recorded in the very voluminous literature on this subject; for this conflict is due less to lack of care in the experimental work than to the fact that some essential factor—the importance of which, however, would not be recognized until the theory had been considered—was not adequately controlled. Indeed a large part of the literature would have been unnecessary, and much painstaking experimental work would have been obviated, if it had been generally recognized that we are here dealing with a fairly mobile equilibrium, and consequently that any change in the factors of the equilibrium is followed by a definite predictable change in the concentration of each of the several molecular species present.

In what follows we shall take up first the general question of the equilibrium in aqueous solutions of carbonates, and consider the quantitative relations existing between the concentrations of the several components at equilibrium. Then we shall go on to discuss the several methods in common use for the determination of CO_2 , combined and free; and finally present some conclusions which follow from the discussion. In what follows it is to be understood that the only basic radical present is assumed to be soda (or potash) and that no other acidic radical is present, since it is impracticable to take up all possible cases; the presence of other bases, such as lime, magnesia, iron, would introduce certain conditions (*e. g.*, by reason of the limited solubility of their carbonates or oxides), which, however, would merely modify the conclusions in a way which can be readily derived for each particular case. Incidentally it may be remarked that some of the conclusions are of importance with respect to any acidimetric titration in which the highest accuracy is desired, by reason of the presence of some carbon dioxide in the liquids to be titrated consequent upon its presence in the air.

I. The Equilibrium in Solutions of Carbonates.

In any aqueous solution containing carbonates, the following relations hold at equilibrium (provided at least that the total concentration of the solution is not excessive—a limitation which is of no consequence in the present instance), it being premised that symbols, such as $[\text{CO}_3^-]$, repre-

sent the molar concentration of the particular molecular species enclosed within the brackets:

$$[\text{H}_2\text{CO}_3] = cP \quad (\text{I})$$

$$\frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = k_1 \quad (\text{II})$$

$$\frac{[\text{H}^+][\text{CO}_3^{--}]}{[\text{HCO}_3^-]} = k_2 \quad (\text{III})$$

Equation I expresses the equilibrium between the undissociated dissolved carbonic acid and the partial pressure P of CO_2 in contact with the solution; II and III define, respectively, the first and second ionization constants of carbonic acid in aqueous solution. There is, moreover, the condition that

$$[\text{B}^+] + [\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{--}] + [\text{OH}^-],$$

where $[\text{B}^+]$ represents the total equivalent concentration of cations present in the solution; in this summation both $[\text{H}^+]$ and $[\text{OH}^-]$ may usually be neglected, as they are small in comparison with the other quantities.

It may be objected that it is beside the mark to consider equilibrium conditions in connection with titrations; but apart altogether from the circumstance that a knowledge of the equilibrium relations constitutes the best means of predicting what will happen in any case, this objection has very little force in this instance by reason of the relative rapidity of the reactions involved. Two only of the reactions require a measurable interval of time: (1) the diffusion of CO_2 from the air space into and through the solution (the rate of this process depends obviously upon the mode of shaking or stirring, but even in an unstirred liquid contained in an open beaker the process is substantially complete in about ten minutes, as evidenced by the change of electric conductance of water left under such conditions); (2) the rate of neutralization,¹ implying that either the hydration of CO_2 or the ionization of H_2CO_3 proceeds slowly. But in this case again, as McBain remarks,

"There is no doubt that the reaction proceeds the greater part of the way in a fraction of a minute; but it is sufficiently incomplete to permit of a bright red color repeatedly vanishing within a few minutes after the first apparent attainment of the end point (with phenolphthalein)."²

¹ J. W. McBain, "The Use of Phenolphthalein as an Indicator. The Slow Rate of Neutralization of Carbonic Acid," *J. Chem. Soc.*, 101, 814 (1912), *q. v.*

² McBain (*Loc. cit.*) demonstrates conclusively that the fading out of the red color of phenolphthalein in nearly neutral solutions is due to the slow neutralization of the carbonic acid in the solution, for in absence of carbonate the end point is instantaneous and permanent; this is therefore a different phenomenon from the fading in presence of strong alkali. This point is obviously of importance in every titration in which phenolphthalein is used as indicator.

Consequently it is here admissible to make use of the relations deduced for complete equilibrium, especially if in any actual case we take into account the effects to be expected from the slow operation of the above two processes; indeed in the usual titration method for determining free CO_2 it is tacitly assumed that this equilibrium adjusts itself during the titration.

By combination of Equations I, II and III we obtain

$$[\text{HCO}_3^-]^2/[\text{CO}_3^{--}] = k_1[\text{H}_2\text{CO}_3]/k_2 = k_1cP/k_2. \quad (\text{IV})$$

It follows, therefore, that, when equilibrium is attained, both the amount of free carbonic acid in solution and the relative proportions of bicarbonate and carbonate ion are determined by the partial pressure of CO_2 in the atmosphere. And it follows, moreover, that a change in P , such as may easily occur when a water is brought from outside into the laboratory, or even in the laboratory from one day to another, will affect all of the quantities, and by amounts which, as we shall see, are not negligible. This is illustrated by experiments recorded by Ellms and Beneker¹ who exposed samples of (a) water, (b) a solution of calcium bicarbonate, to the air of the laboratory, with the following results, expressed in parts per million:

	(a).	(b).		
	Free CO_2 .	"Free CO_2 ."	"Half bound."	"Fixed."
Original.....	0	52.8	109.4	109.4
After 24 hrs.....	2.2	7.0
After 48 hrs.....	14.1 ²	1.1
After 72 hrs.....	0.9	0	80.7	84.5

From this one can readily see the possibilities of variation in the amount of free CO_2 in solution—and, consequently, as we shall see, upon the proportion of bicarbonate to carbonate and the degree of alkalinity of the solution—especially when the amount is in excess of that demanded by the equilibrium; for, as was pointed out by McCoy,³ and since then by others, low results are invariably attained if such solutions, contained in a beaker, are exposed even for four or five minutes.

The values of k_1 , k_2 and c depend upon the temperature, and c also depends upon the total concentration of base $[\text{B}]$. For the present purpose it suffices to consider a single temperature, which for convenience has been chosen to be 25° ; all calculations in this paper refer to 25° , but a variation of a few degrees away from 25° would make no essential difference in the results. The values of c at 25° for several values of $[\text{B}]$ are as follows:⁴

¹ THIS JOURNAL, 23, 407 (1901).

² On this day a CO_2 generator was being used in the laboratory.

³ McCoy, *Am. Chem. J.*, 29, 444 (1903).

⁴ On the basis of Bohr's measurements on water and solutions of NaCl (*Ann. Physik*, 68, 500 (1899)). c decreases with rise of temperature; at 100° it is only 0.011 (Bohr and Bock, *Ibid.*, 44, 342 (1891)), so that at 100° the concentration of H_2CO_3 would be, ceteris paribus, one-third as great as at 25° .

[B].....	0	0.1	0.2	0.3	0.5	1.0
c	0.0338	0.329	0.321	0.314	0.300	0.270

Now the average proportion of CO_2 in the atmosphere is not far from 3 parts per 10,000 (*i. e.*, $P = 0.0003$); but the air of a laboratory will usually contain 4 or 5 parts, and this proportion may range up to 10 or 12, or in especially ill ventilated rooms to still higher values. The concentration of H_2CO_3^1 (*i. e.*, of free CO_2) in any dilute solution in equilibrium at 25° with an atmosphere containing CO_2 at P is, in accordance with Equation I, as follows:

$P \times 10^4$	3	4	5	6	8	10
$[\text{H}_2\text{CO}_3] \times 10^4$	1.0	1.3	1.7	2.0	2.7	3.3
CO_2 , parts per million.....	0.44	0.59	0.73	0.9	1.2	1.5

Thus the concentration of free CO_2 in any solution in *equilibrium* with laboratory air would be about 1 part per million, or more in certain cases; if the concentration actually present is larger or smaller than corresponds to equilibrium, the solution will tend to give off, or absorb, CO_2 , and will actually do so unless due precautions are taken to prevent it.

Let us now consider the relative proportions of bicarbonate and carbonate in relation to the partial pressure P of CO_2 . The proportion of sodium (or indeed of any univalent base) associated with bicarbonate can be calculated by means of Equation IV if the ratio k_1/k_2 and the degree of ionization of $\text{NaHCO}_3(\gamma_1)$ and of $\text{Na}_2\text{CO}_3(\gamma_2)$ are known. The calculation of k_1/k_2 from the experimental results on which it is based involves γ_1 and γ_2 ; heretofore, for want of a better method, the assumption has been made that γ_1 and γ_2 are identical with the degree of ionization of sodium acetate and of sodium sulfate, respectively (salts of the same ionic types) an assumption which, however, led to different values of k_1/k_2 at different concentrations of total base.² Now Seyler and Lloyd³ have shown on the basis of McCoy's work, and also of new experiments in more dilute solutions, that a constant value of k_1/k_2 (*viz.*, 7100) is obtained by assigning smaller values to γ_2 , as follows:

[Na].....	0.05	0.1	0.2	0.3	0.5	1.0
γ_1	0.82	0.78	0.73	0.69	0.64	0.52
γ_2	0.56	0.46	0.37	0.31	0.24	0.14

¹ In identifying $[\text{H}_2\text{CO}_3]$ with the total concentration of free CO_2 in solution we are tacitly assuming that all the CO_2 —apart from the ionized portion—exists as the hydrated form in solution; this assumption is the best that can be done at present, but introduces no error which is significant in the present connection. This point, and a number of others touched upon in the present paper, have been more fully considered previously (THIS JOURNAL, 37, 2001 (1915)), *q. v.*

² See McCoy, *Am. Chem. J.*, 29, 437 (1903), or the recalculation of McCoy's results by Johnston (THIS JOURNAL, 37, 2001 (1915)). Professor Stieglitz pointed out in a letter to me that the true degree of ionization of Na_2CO_3 is in all probability much less than that of Na_2SO_4 .

³ See footnote 1, p. 947.

"These values represent the activity of sodium carbonate (as regards the CO_3 ion) and of sodium bicarbonate in equilibrium with each other and with carbonic acid. Those for γ_1 are founded upon the ionization of sodium acetate calculated from the conductivity. The values for γ_2 are much less than would be expected from analogy with sodium sulfate, even after allowing for the presence of an intermediate ion."¹ And they proceed to show how these values of γ_2 are in harmony with many facts as to the behavior of carbonate solutions and serve to reconcile data hitherto apparently in conflict. We shall, therefore, adopt these values as the best available at the present time for the purpose in hand, and calculate the partial pressure P of CO_2 in equilibrium at 25° with various proportions of bicarbonate and carbonate in a solution 0.1 N with respect to total sodium. If the concentration of sodium as bicarbonate is b , then²

$[\text{HCO}_3^-] = b\gamma_1 = 0.78b$ and $2[\text{CO}_3^{--}] = (0.1 - b)\gamma_2 = 0.46(0.1 - b)$; and from Equations IV and I

$$[\text{HCO}_3^-]^2/[\text{CO}_3^{--}] = k_1[\text{H}_2\text{CO}_3]/k_2 = 7100[\text{H}_2\text{CO}_3] = 234 P.$$

Values of P calculated in this way for several values of b are presented in Table I.³

TABLE I.—THE PARTIAL PRESSURE OF CO_2 IN EQUILIBRIUM WITH, AND THE ALKALINITY OF, SEVERAL BICARBONATE-CARBONATE SOLUTIONS, 0.1 N WITH RESPECT TO TOTAL SODIUM; TEMPERATURE 25° .

% bicarbonate.	[Na] as NaHCO_3 . b .	[Na] as Na_2CO_3 . $0.1 - b$.	$[\text{HCO}_3^-]$ $= b\gamma_1$.	$2[\text{CO}_3^{--}]$ $= (0.1 - b)\gamma_2$.	$P \times 10^4$.	$[\text{OH}^-] \times 10^4$.
35	0.035	0.065	0.0273	0.0299	2.14	9.3
40	0.040	0.060	0.312	0.276	3.01	7.5
45	0.045	0.055	0.351	0.253	4.16	6.1
50	0.050	0.050	0.390	0.230	5.65	5.0
55	0.055	0.045	0.429	0.207	7.60	4.1
60	0.060	0.040	0.468	0.184	10.18	3.3
65	0.065	0.035	0.507	0.161	13.65	2.7

This shows the large influence which a change in the proportion of CO_2 in the air, such as may readily take place in a short time in a laboratory, exerts upon the position of the equilibrium carbonate-bicarbonate in solutions 0.1 N with respect to base;⁴ the change produced by a given change

¹ Quoted from the manuscript of Seyler and Lloyd.

² The real value of γ_1 and of γ_2 would vary slightly with b by reason of the change in the concentration of NaHCO_3 and Na_2CO_3 ; but neglect of this variation causes no error which is significant in the present connection.

³ McCoy (*Loc. cit.*) has made a similar calculation.

⁴ It is obvious that the above results hold equally for any univalent base, since the degree of ionization of all salts of the same valence type is substantially identical (see, e. g., Noyes and Falk, *THIS JOURNAL*, 34, 475 (1912)); moreover they would be substantially correct for any base.

in P is inversely proportional approximately to the square root of the total concentration, so that, *e. g.*, in a 1.0 N solution the percentage change would be just about one-third as much as in the 0.1 N solution.¹ The complete establishment of this equilibrium requires some time; thus McCoy,² who passed a current of outside air through a solution of (a) NaHCO_3 , (b) Na_2CO_3 , each 0.1 N with respect to sodium and at 25°, found that the same condition (*viz.*, 40.4% bicarbonate) was reached in either solution in about three days. But though a period of three days is required for the attainment of a state of equilibrium, an interval of a few minutes suffices to bring about a marked change in the proportion of bicarbonate to carbonate (and hence in alkalinity of the solution); this is well illustrated by another experiment of McCoy's, who passed air through a 0.1 N solution originally made up from solid bicarbonate, and examined the rate of change of the proportion, with the following results:

Time in hours.....	0	0.25	0.67	1.17	2.0	26	48	72
% Na as bicarbonate.....	95	88	80	76	75	45	43	40

This rate depends, of course, upon the mode of experiment; in any case the above illustration suffices to show that material changes in the proportion may result from exposure of the solution for even a few minutes to an atmosphere other than that with which it is in equilibrium.

From the foregoing it is obvious that most solutions, natural waters especially, which we wish to analyze will have reached substantially the equilibrium state,³ consequently it is altogether unnecessary to determine the concentration of each of the several constituents, because if two of them are known, the others can be calculated. Moreover the proportion $[\text{HCO}_3^-]/[\text{CO}_3^{--}]$ absolutely determines the alkalinity of the solution, and conversely; for by Equation III

$$[\text{H}^+] = k_2[\text{HCO}_3^-]/[\text{CO}_3^{--}] = 4.8 \times 10^{-11} [\text{HCO}_3^-]/[\text{CO}_3^{--}] \text{ at } 25^\circ \text{ and}$$

¹ The actual percentage of bicarbonate for a given value of P is of course also dependent upon the concentration, as is evident from the form of Equation IV, becoming smaller as the total concentration of base increases.

² *Am. Chem. J.*, 29, 459 (1903). The results indicate that the proportion of CO_2 in the air passed through was about 3.0 parts per 10,000. Likewise one can deduce that the air passed through their carbonate-bicarbonate solutions by Cameron and Briggs (*J. Phys. Chem.*, 5, 537 (1901)) contained from 5 to 7 parts CO_2 per 10,000 and hence was presumably laboratory air.

³ For purely scientific purposes there would seem to be little to be gained by determinations of the concentration of the several constituents present in a solution which has not attained substantially to a state of equilibrium.

⁴ According to Walker and Cormack (*J. Chem. Soc.*, 77, 8 (1900)) $k_1 = 3.04 \times 10^{-7}$ at 18°; whence, by means of the van't Hoff formula, on the basis that the heat change accompanying the reaction is 2700 cal., $k_1 = 3.39 \times 10^{-7}$ at 25° (see Lewis and Randall, *THIS JOURNAL*, 37, 467 (1915)), and $k_2 = 3.39 \times 10^{-7}/7100$. In strictness the experimental datum 3.04×10^{-7} represents the value at 18° of the expression $[\text{H}^+][\text{HCO}_3^-]/([\text{H}_2\text{CO}_3] + [\text{CO}_2]_s)$; but we do not know what fraction of the total CO_2 in solution

since $[H^+][OH^-] = K_w = 0.8 \times 10^{-14}$ at 25°

$$[OH^-] = 1.7 \times 10^{-4} [CO_3^{2-}] / [HCO_3^-] \text{ at } 25^\circ. \quad (IIIa)$$

Alternatively by combination of Equations I, II and III, we obtain:

$$[H^+][HCO_3^-] = k_1 cP = 3.39 \times 10^{-7} cP \text{ at } 25^\circ \quad (V)$$

and

$$[H^+]^2 [CO_3^{2-}] = k_1 k_2 cP = 1.66 \times 10^{-17} cP \text{ at } 25^\circ. \quad (VI)$$

Hence, if we know P and the total equivalent amount of CO_2 in the solution, we can determine $[OH^-]$; for example in a carbonate-bicarbonate solution which is 0.1 N with respect to sodium the alkalinity for several values of P is given in the last column of Table I.² This emphasizes again the fact that these several quantities are not independent variables; that it suffices to fix two of them only in order to define completely the constitution of the solution.

But for our present purpose it is better to consider the relation between the alkalinity of the solution and the concentration of free CO_2 (which, it will be recalled, determines the proportion of bicarbonate to carbonate); for knowledge of this relation, which is readily derived, is essential to the understanding of any titration process in which carbonic acid in any form is present. By combining the condition $[B^+] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$, where $[B^+]$ is the total equivalent concentration of ionized base, with Equations II, III and the relation $[H^+][OH^-] = K_w$, we obtain

$$([B^+] + [H^+])[H^+]^2 - (k_1[H_2CO_3] + K_w)[H^+] - 2k_1k_2[H_2CO_3] = 0$$

whence

$$[H_2CO_3] = \frac{([B^+] + [H^+])[H^+]^2 - K_w[H^+]}{k_1[H^+] + 2k_1k_2} = \frac{([B^+] + [H^+])[H^+]^2 - 8 \times 10^{-16}[H^+]}{3.4 \times 10^{-7}[H^+] + 3.3 \times 10^{-17}} \text{ at } 25^\circ.$$

exists as H_2CO_3 , except that it is probably more than one-half. This point is more fully considered in a previous paper (THIS JOURNAL, 37, 2001 (1915)); in the present paper it is presumed that all the uncombined CO_2 in solution exists as H_2CO_3 .

¹ This is undoubtedly the most accurate value now available (see Lewis and Randall, THIS JOURNAL, 36, 1979 (1914)). Neglect of the contact potentials is of itself sufficient to account for the higher value given by Frary and Nietz (THIS JOURNAL, 37, 2263 (1915)); their use of this higher value in interpreting their further experiments is however perfectly justified.

² For similar calculations for solutions of carbonates of calcium and magnesium see Johnston, THIS JOURNAL, 37, 2012, 2016 (1915); Johnston and Williamson, *Ibid.*, 38, 975 (1916); cf. also Auerbach and Pick, "Die Alkalinität wässriger Lösungen kohlensaurer Salze," *Arbeiten kais. Gesundheitsamt*, 38, 243 (1911); in their equations, however, as in those of Frary and Nietz (THIS JOURNAL, 37, 2268 (1915)), the assumption is implicit that the solution neither gains nor loses CO_2 , which would require that the experiments be carried out in closed vessels completely filled with liquid, and consequently some of their conclusions do not necessarily hold for all cases.

This formula¹ allows us to calculate values of $[H_2CO_3]$ for any value of $[B^+]$ and $[H^+]$ —in other words to calculate the concentration of free CO_2 (and hence the ratio of bicarbonate to carbonate) in a solution of any total concentration at the end point registered by any indicator. A series of such calculations have been carried out, the results of which are presented in Table II, to which it may here be remarked that indicators which change color at values of $[H^+]$ greater than 10^{-6} are—as is obvious from the table—insensitive towards ordinary amounts of CO_2 , and that the higher concentrations of H_2CO_3 are unlikely to occur in ordinary practice, since even 10 parts CO_2 per million would require a partial pressure in the atmosphere of about 0.007 (*i. e.*, 70 parts in 10,000) to prevent the solution from losing any CO_2 .

By means of this table, in conjunction with a table of indicator constants,² one is enabled to choose an indicator and to conduct any titration of a carbonate solution so that the error from the free CO_2 still in solution at end point shall not exceed a certain limit. As an example, if the untitrated CO_2 must be less than 1 part per million, and the total concentration of base at the end point is 0.001, one must choose an indicator at a concentration such that the color change takes place when $[H^+]$ is between 10^{-6} and 10^{-9} —*e. g.*, phenolphthalein at the proper concentration.³ To this question we shall revert when we take up the several methods; but before doing so, we shall consider a few other general points, affecting all of the methods, which follow directly from the various principles which we have discussed.

The illustrations presented in the preceding pages demonstrate the futility of attempting to determine the real proportions of free CO_2 , or of carbonate and bicarbonate, in any solution, unless special precautions be taken to ensure that no change can take place during the manipulations, from the collection or preparation of the sample onwards. It is

¹ An analogous formula has been given by Prideaux (*Proc. Roy. Soc.*, (A) 91, 535 (1915)) who has used it to calculate the acidity of carbonate solutions for several values of $[H_2CO_3]$ and $[B]$.

² The most complete tables are given in papers by Sørensen (*Biochem. Z.*, 21, 131 (1909); 22, 353 (1909); 24, 381 (1910)). For some data, and references to others, see A. A. Noyes "Quantitative Application of the Theory of Indicators to Volumetric Analysis," *THIS JOURNAL*, 32, 815 (1910); see also Walpole, *Biochem. J.*, 8, 628 (1914); Lubs and Clark, *J. Wash. Acad.*, 5, 609 (1915). A very good discussion of indicators and their properties will be found in "Die Theorie der alkalimetrischen und azidimetrischen Titrierungen," by N. Bjerrum (*Ahrens' Sammlung*, 21, Heft 1-3 (1914)); it should be consulted by all who are interested in the definitive accuracy of titration methods. In this pamphlet, which was brought to my attention by Dr. R. C. Wells after the present paper was completed, Bjerrum also takes up some of the problems considered in the following pages.

³ On this point see Rosenstein, "The Ionization Constant of Phenolphthalein and the Effect upon it of Neutral Salts," *THIS JOURNAL*, 34, 117 (1912).

TABLE II.—THE CONCENTRATION OF FREE CO_2 , EXPRESSED IN (a) MOLES PER LITER (b) PARTS PER MILLION, WHICH WOULD BE IN EQUILIBRIUM WITH THE HYDROGEN-ION CONCENTRATION $[\text{H}^+]$ AT THE TOTAL EQUIVALENT ION-CONCENTRATION OF BASE $[\text{B}^+]$.

[B ⁺].	[H ⁺]						
	10 ⁻⁹ .	10 ⁻⁸ .	10 ⁻⁷ .	10 ⁻⁶ .	10 ⁻⁵ .	10 ⁻⁴ .	10 ⁻³ .
0.....	$\begin{cases} a \\ b \end{cases}$	5.8×10^{-9}	2.9×10^{-9}
0.0001.....	$\begin{cases} a \\ b \end{cases}$	0.00025	0.13
0.001.....	$\begin{cases} a \\ b \end{cases}$	3.0×10^{-9}	3.5×10^{-7}	2.9×10^{-6}	2.9×10^{-4}
0.01.....	$\begin{cases} a \\ b \end{cases}$	5.5×10^{-10}	0.00013	0.015	0.13	13
0.1.....	$\begin{cases} a \\ b \end{cases}$	6.0×10^{-11}	0.000024	1.4×10^{-7}	3.7×10^{-6}	2.9×10^{-5}	2.9×10^{-3}
1.0.....	$\begin{cases} a \\ b \end{cases}$	0.0000026	2.5×10^{-8}	0.0062	0.16	13	130
	$\begin{cases} a \\ b \end{cases}$	2.8×10^{-9}	0.0011	1.5×10^{-6}	3.7×10^{-5}	2.9×10^{-4}	2.9×10^{-2}
	$\begin{cases} a \\ b \end{cases}$	0.00012	2.7×10^{-7}	0.066	1.6	130	1300
	$\begin{cases} a \\ b \end{cases}$	3.0×10^{-8}	0.012	1.5×10^{-6}	3.7×10^{-4}	2.9×10^{-3}	2.9×10^{-1}
	$\begin{cases} a \\ b \end{cases}$	0.0013	2.7×10^{-8}	0.66	16	130	13000
	$\begin{cases} a \\ b \end{cases}$		0.12	1.5×10^{-4}	3.7×10^{-3}	2.9×10^{-2}	2.9
	$\begin{cases} a \\ b \end{cases}$			6.6	160.	1300	130000

to be borne in mind that any titration (or other) method of analysis of a solution containing combined CO_2 can yield information only as to the total amount of the particular constituent present up to the end of the titration—an amount which bears no necessary relation to that originally present unless the solution be preserved in bottles absolutely filled and tightly sealed and all the manipulations be carried out expeditiously. Likewise any solution to be used as a standard—*e. g.*, a solution of Na_2CO_3 for the determination of free CO_2 —must either be freshly prepared or kept in a vessel arranged so that the solution withdrawn is automatically replaced by mercury or some other immiscible liquid in which CO_2 is not soluble; and any manipulations with such a solution must be performed as quickly as possible, and in such a way that the gas space in contact with it is kept small. The necessity of precautions of this kind has been discovered in practice; for instance by Lunge,¹ also by Tillmanns and Heublein² who recommend that a preliminary titration be made and that then the exact titration, which must be carried out in a closed flask containing as little air as is compatible with the manipulations, be made rapidly by adding nearly the right amount, shaking and then bringing to the end point. Rapid titration is advisable for another reason—namely, that addition of any solution to a solution containing combined CO_2 of itself changes the state of equilibrium, the adjustment of which condition is, as we have seen, not instantaneous; errors due to this source can be minimized by rapid titration, and by the addition of a salt with a common ion,³ which is effective because it sets back the ionization of the carbonates and in this way reduces the rate of the reaction $\text{CO}_3^{2-} + \text{H}_2\text{CO}_3 = 2\text{HCO}_3^-$.

The necessity of these precautions has been emphasized here because the standard text-books of quantitative analysis pay little or no attention to them. Neglect of them, even in work otherwise very carefully done, is responsible for glaring inconsistencies in published analyses; but it would be invidious to single out an instance from so many.

We shall now proceed to the discussion of particular applications and illustrations of the general principles we have outlined. To discuss all of the possible cases is, of course, impracticable; so I have taken up only those methods which are in common use and, for the sake of simplicity, have considered that the only bases present are alkali metals.

II. Estimation of the Total Base in Alkalies Containing Carbonate.

When an alkali containing carbonate is titrated with acid, and methyl

¹ See *postea*, p. 964.

² Tillmanns and Heublein, *Z. Nahr. Genussm.*, 20, 617 (1910).

³ This course also is recommended by Lunge. Such an addition will at the same time have a slight effect on the relative proportion of base associated with carbonate and bicarbonate.

orange as indicator,¹ there is some uncertainty as to when the end point is reached because there is a gradual reddening as the true end point is approached. Küster² showed how this difficulty can be overcome, and demonstrated by careful experimental work that his method of determining the end point yields reproducible and accurate results. A false impression prevails quite commonly that CO_2 is without effect upon methyl orange; but, as a matter of fact, a current of CO_2 will change the color of this indicator to a reddish yellow and this shade persists for a long time if the solution is preserved in a closed flask or in such a way as to prevent loss of CO_2 . This color change is, of course, due to the presence of H^+ . During the titration of carbonate solutions the concentration of H^+ is so small as not to begin to affect methyl orange until the titration is very nearly complete, *i. e.*, until the concentration of HCO_3^- and CO_3^{2-} are very small. As the last portions of acid are added, the concentration of H^+ increases very slowly until, when the amount of acid just equivalent to the soda has been added, it is practically the same as in a solution of CO_2 in water and consequently the colors in the two cases are identical; a further drop of acid now produces a sudden increase in $[\text{H}^+]$, and consequently a sudden color change. Accurate and definite results can, therefore, be obtained by titrating until the solution is of the same shade as a comparison solution made by passing CO_2 into water containing the same proportion of methyl orange. The accuracy of the results obtained by the use of such a comparison shade is attested by the work of Küster³ who made up two solutions—one of NaOH which proved to be altogether free from CO_3 ,⁴ a second of Na_2CO_3 which contained no appreciable quantity of either hydroxide or bicarbonate—and titrated various mixtures of the two with the following results:

Cc. taken.		Cc. 0.5 N acid.	
NaOH.	Na_2CO_3 .	Used.	Calc.
15	30	66.65	66.66
15	20	57.28	57.28
15	10	47.95	47.91
15	5	43.31	43.22
15	2	40.41	40.41
15	..	38.54 ⁵	38.53

¹ This is sometimes called the *Hehner method*, sometimes (especially in German) the *Lunge method*; according to Lunge himself (*Chem. Tech. Untersuchungsmethoden*, 1, 838 (1904)) he was the first to publish it in 1885.

² F. W. Küster, "Kritische Studien zur volumetrischen Bestimmung von Alkalikarbonaten, sowie über das Verhalten von Phenolphthalein und Methylorange als Indikatoren," *Z. anorg. Chem.*, 13, 127 (1897), q. v.

³ *Loc. cit.*, p. 147.

⁴ Incidentally it may be remarked that the presence of small quantities of CO_2 in solutions of alkali hydroxide will not necessarily be detected merely by addition of barium chloride, as Küster (*Loc. cit.*, p. 134) remarked; for a small quantity of BaCO_3 will not precipitate when the concentration of NaOH is high.

⁵ No comparison at all was necessary in this case. Each datum is the mean of three concordant titrations.

By means of this simple precaution, then, the results are accurate; if it is neglected, the uncertainty may be as much as 0.5% of the total amount of base actually present.

Ellms,¹ presumably in an endeavor to obviate this uncertainty, used lacmoid, phenacetoline, or erythrosine as indicators in a series of titrations, but found that the color change occurs when only 98–99% of the base actually present has been neutralized. This result could now be predicted from the constants of these indicators, all of which change color at too small a concentration of H^+ for the purpose in hand; it may be possible to select another indicator somewhat more suitable for this purpose than methyl orange, although it is to be expected that no indicator will yield any more accurate results except a similar comparison method be used.²

III. Estimation of the Free Alkali in Liquids Containing Carbonates.

Küster³ observed relatively large differences between the results of titrations of alkali containing carbonate carried out according to the procedures recommended in various text-books; in order to ascertain which of these methods yields correct results he made a careful comparison of them. To this end he made a series of analyses of an alkali solution (A) about 2 *N*, precipitating with a 10% solution of $BaCl_2$ and titrating back with acid and phenolphthalein until the solution was colorless; his results are as follows, each figure being the mean of three separate titrations which did not differ among themselves by more than 0.05 cc.:

Procedure.	Cc. 0.5 <i>N</i> acid used.	Percentage of total Na as carbonate.
10 cc. A titrated directly, with methyl orange to normal color	42.49	..
I. 20 cc. A + 20 cc. $BaCl_2$; filtered; 20 cc. filtrate (= 10 cc. A) titrated	33.61	20.9
II. 20 cc. A + 50 cc. H_2O + 20 cc. $BaCl_2$ + 10 cc. H_2O ; filtered; 50 cc. filtrate (= 10 cc. A) titrated	33.90	20.2
III. 20 cc. A + 150 cc. H_2O + 20 cc. $BaCl_2$ + 10 cc. H_2O , filtered; 100 cc. filtrate (= 10 cc. A) titrated	34.01	20.0
IV. 20 cc. A + 15 cc. H_2O + 20 cc. $BaCl_2$ + 10 cc. H_2O ; 100 cc. liquid (not filtered) titrated	34.39	19.1
V. 10 cc. A + 50 cc. hot H_2O + 10 cc. $BaCl_2$; filtered and ppt. well washed; total filtrate titrated	34.50	18.8
VI. 10 cc. A + 100 cc. H_2O + 10 cc. $BaCl_2$; allowed to stand, titrated without being filtered	34.72	18.3
VII. 10 cc. A titrated directly, with phenolphthalein until colorless	38.58	18.4

The low result—corresponding to too great an apparent percentage of carbonate—of Procedures I–IV, Küster attributes to absorption of alkali

¹ J. W. Ellms, *THIS JOURNAL*, 21, 359 (1899).

² See also Norton and Knowles, *THIS JOURNAL*, 38, 877 (1916).

³ *Z. anorg. Chem.*, 13, 127 (1897).

by filter paper and precipitate and to absorption of CO_2 by the solution in the course of the manipulations. That the results obtained by Procedure VI are correct he shows by similar titration of known mixtures of (a) a solution of NaOH entirely free from CO_2 with (b) a freshly prepared solution of Na_2CO_3 which contained no appreciable quantity of either hydroxide or bicarbonate:

Cc. taken.			Cc. 0.5N acid.	
NaOH .	Na_2CO_3 .	BaCl_2 .	Used.	Calculated.
15	30	30	38.51	38.53
15	20	20	38.52	
15	10	10	38.54	
15	5	10	38.53	
15	2	10	38.52	
15	..	10	38.55	

From this it is obvious that this method, which, since filtration is omitted, is at the same time the simplest to carry out, yields correct results for the free alkali, which are independent of the proportion of carbonate present in the solution. On the other hand, it is claimed by Bruhns¹ that the precipitated BaCO_3 is attacked to a slight extent by the acid used to titrate the excess of hydroxide, with consequent small errors in the results; to obviate which he filters off the precipitate in a special funnel arranged so that the filtrate does not come in contact with the air. There is little question that such a source of error is quite possible; yet by allowing the precipitate to settle completely and then by careful manipulation during the titration it should be easily practicable to render this error negligible, as indeed it appears to be in Küster's work. Again,² Sørensen and Andersen made a series of very carefully controlled experiments in which, however, they allowed only ten minutes for the settling of the precipitate and titrated to the same pink color as a comparison solution containing BaCO_3 and the same amount of phenolphthalein; and found that this method yields slightly too high results for the alkalinity,³ but accurate

¹ G. Bruhns, *Z. anal. Chem.*, **45**, 473 (1906). As a partial protection against the air he uses a layer of benzene. A film of ether was used for this purpose by Stransky (*Chem. Ztg.*, **9**, 100 (1908)).

² S. P. L. Sørensen and A. C. Andersen, *Z. anal. Chem.*, **47**, 279 (1908).

³ This they attribute to the formation of a small quantity of $\text{Ba}(\text{HCO}_3)_2$. If too much hydroxide is present, some basic carbonate is, according to the authors, precipitated in cold solution; solutions containing bicarbonate obviously should not be heated. But these difficulties can be surmounted by addition of substantially the equivalent amount of acid or NaOH respectively before the heating and subsequent precipitation by means of BaCl_2 . Sørensen and Andersen prove, therein confirming Guth (*Gesundheitsingenieur*, **31**, 737 (1908)), that the assertion of Le Blanc and Novotny (*Z. anorg. Chem.*, **51**, 181 (1906); repeated *Ibid.*, **53**, 344 (1907)) to the effect that addition of BaCl_2 to a 0.1 N solution of Na_2CO_3 results in a slightly acid solution, is untrue so long as the sodium carbonate is free from bicarbonate. The greater part

results if the precipitation is carried out in hot solution, provided that the original solution was mainly carbonate. Nevertheless, in the opinion of the writer, this conclusion, though applicable to this particular procedure, does not hold if several hours be allowed to elapse between precipitation and titration and particularly if titration with acid is continued until the solution is colorless; for from the theory of the method (developed in the next section) it follows that we must titrate in such a way as to determine the total amount of OH^- present in the solution after the precipitate of BaCO_3 has separated out, and hence must continue until the indicator has ceased to show pink.

The seventh method—direct titration with acid and phenolphthalein as indicator—is not to be recommended. For, as was shown by Küster, and also independently by Lunge,¹ the result depends greatly on what one chooses as the point at which the solution is considered to have become colorless;² it may well be 4% too high, though this amount is diminished in presence of sodium chloride.³ On the other hand Seyler⁴ found, as the result of a series of careful titrations, that this error is due chiefly to a loss of CO_2 ; and Tillmanns and Heublein⁵ showed directly that in such titrations the solution loses CO_2 ,⁶ and on carrying out titrations in closed flasks observed sharper end points and were able to obtain good results. Nevertheless this method could yield correct results only if titration were continued until a certain shade was reached, but, since this proper depth of shade is not invariable but depends upon the concentration and constitution of the solution,⁷ this course would be impracticable if the highest accuracy is desired.

of this confusion is directly due to a failure to recognize that there is *equilibrium* between the several molecular species.

¹ G. Lunge, *Z. angew. Chem.*, 10, 41 (1897).

² This is the same phenomenon as is discussed at length in Section V.

³ This was also observed by Lunge and Lohhöfer, *Z. angew. Chem.*, 14, 1125 (1901). The reason for this action is that the added salt sets back the ionization of the carbonate and bicarbonate, and hence diminishes the speed of readjustment of the equilibrium. For this reason, too, titration with a solution of KHSO_4 , as suggested by Cameron (*Am. Chem. J.*, 23, 471 (1900)) will, other things being equal, yield closer results than titration with a simple acid.

⁴ C. A. Seyler, *Analyst*, 22, 314 (1897).

⁵ Tillmanns and Heublein, *Z. angew. Chem.*, 24, 874 (1911).

⁶ Absorption of CO_2 by the solution may occur in certain cases, particularly in natural waters which have been diluted with distilled water—a procedure which may well yield misleading results with respect to the composition and properties of the undiluted water; for instance, the alkalinity of the diluted water is not a direct measure of that of the undiluted water.

⁷ This deduction is confirmed by the experimental work recorded by Seyler in "Studies of the Carbonates IV" (see note, p. 947). Correct results could of course be attained by suitable calibration of the method, as Seyler proposes; but it seems simpler to follow the procedure recommended by Küster.

IV. Estimation of Both Carbonate and Bicarbonate.

The method most commonly used for this determination—*viz.*, to titrate until phenolphthalein is colorless, to add methyl orange and continue the titration until the color change is observed—is not to be recommended where any accuracy is desired. For, as we have seen, the uncertainty as to the proper end point with phenolphthalein in presence of carbonates is such that there may be an error of 5% in this portion of the titration—an error which may cause a very large percentage error in the proportion of bicarbonate since the latter is obtained by difference. According to Tillmanns and Heublein,¹ somewhat better results can be obtained either by titrating in a closed flask, or by proceeding as follows: Determine the amount of acid required to bring about the color change with methyl orange as indicator, then to a separate portion of the solution add this amount of acid and titrate back with NaOH, until phenolphthalein just shows a pink color.

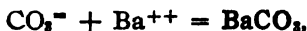
But, for reasons already given, none of these methods, as ordinarily carried out, is trustworthy; moreover they are unnecessary since there is an equally simple procedure which is reliable. The total alkali is determined as before by titration with methyl orange to the "normal" color of a comparison solution.² In order to ascertain the proportion of bicarbonate,³ one adds the solution to a known excess of standard alkali, previously mixed with excess of barium chloride, sets aside until the precipitate has settled, and, without filtering, titrates, using phenolphthalein, until the solution is colorless; the alkali used up corresponds to the bicarbonate present. The following figures, due to Küster, attest the accuracy of this method; for the difference in the amount of acid used is proportional to the added amount of a mixed carbonate-bicarbonate solution:

Cc. taken.		Cc. 0.5N acid.	
NaOH.	$\begin{cases} \text{Na}_2\text{CO}_3 \\ \text{NaHCO}_3 \end{cases}$	Used.	Difference.
15	..	38.53
15	5	37.92	0.61 = 5 × 0.122
15	10	37.30	1.23 = 10 × 0.123
15	30	34.80	3.73 = 30 × 0.124

That this method should yield accurate results follows also from a consideration of the theory of the method. Besides the reaction:



or better,

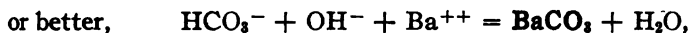
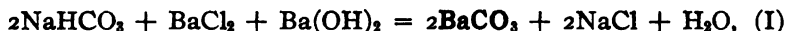


¹ Tillmanns and Heublein, *Z. anorg. Chem.*, 24, 874 (1911).

² See Section II.

³ Compare Section III. Confirmatory evidence of the accuracy of this procedure is offered by McCoy (*Am. Chem. J.*, 29, 444 (1903)). Care must be taken that no free CO_2 is lost during the manipulations.

which is accompanied by no change in the alkalinity¹ of the solution, there are the two reactions



whence it follows that one equivalent of OH^- disappears for each equivalent of HCO_3^- taken out of solution (as BaCO_3) and for each equivalent of free H_2CO_3 present originally. When the precipitation is complete—*i. e.*, before the excess of alkali has been titrated back—the following equilibrium equations² hold:

$$[\text{Ba}^{++}][\text{CO}_3^{--}] = K_B = 7 \times 10^{-9} \quad (a)$$

$$[\text{H}^+][\text{CO}_3^{--}] = k_2[\text{HCO}_3^-] = 4.8 \times 10^{-11}[\text{HCO}_3^-] \quad (b)$$

whence we obtain

$$[\text{HCO}_3^-] = \frac{K_W K_B}{k_2 [\text{OH}^-] [\text{Ba}^{++}]} = \frac{10^{-13}}{[\text{OH}^-] [\text{Ba}^{++}]}.$$

Consequently, the greater the concentrations of $[\text{OH}^-]$ and $[\text{Ba}^{++}]$ are at this point, the smaller will be the concentration of residual bicarbonate, *i. e.*, of bicarbonate which will remain untitrated. In other words, the error of this method can be made as small as we please by having excess of both $[\text{OH}^-]$ and $[\text{Ba}^{++}]$ present when precipitation is complete.

As an illustration let us make an approximate calculation of a titration recorded by McCoy.³

9.94 cc. of a carbonate-bicarbonate solution, 0.1 *N* with respect to sodium, was run into 7.49 cc. 0.1 *N* Ba(OH)_2 and 2 cc. 0.5 *N* BaCl_2 and the residual free alkali required 0.70 cc. 0.1 *N* HCl . The total barium present initially was 0.00175/2 mols; that used up, which is equivalent to the total sodium, was 0.000994/2 mols; so that the total barium present in the 20 cc. at the end was 0.00076/2 mols., and therefore $[\text{Ba}^{++}] = 0.019$.⁴ The OH^- remaining (that is, before the titration with acid) was equivalent to 0.70 cc. 0.1 *N* acid, and therefore $[\text{OH}^-] = 0.0035$. By substitution of these values in the above expression, we find that

$$[\text{HCO}_3^-] = \frac{10^{-13}}{1.9 \times 10^{-2} \times 3.5 \times 10^{-3}} = 10^{-8}$$

consequently the HCO_3^- remaining untitrated is negligible—in other words the method yields correct results.

This method then, when carried out as outlined above, yields correct results for the proportion of bicarbonate to carbonate present in the solution at the time of analysis, provided that the only metals present

¹ This of course refers only to the carbonate which is present as such in the solution, and does not imply that there is no change in alkalinity when BaCl_2 is added to an actual solution of alkali carbonate.

² (a) is the solubility product constant of barium carbonate at 16° (Johnston, *THIS JOURNAL*, 37, 2019 (1915)); (b) is Equation III of the present paper.

³ *Am. Chem. J.*, 29, 448 (1903).

⁴ For the sake of simplicity we assume here that ionization is complete.

are those with soluble hydroxides; otherwise, a correction must be made for the equivalent alkalinity of the insoluble hydroxide or "basic salt" precipitated upon addition of the baryta. This correction, which is discussed in the text-books, is necessary in many cases, since most natural waters contain magnesia and some contain iron; its application always detracts from the accuracy of the method because one cannot ensure that some part of the insoluble base is not precipitated as an indefinite "basic salt." In any case it is to be borne in mind that a reliable method of analysis yields useful results only if due precautions in preparing (or sampling) and preserving the solution have been taken. As an illustration of some of these points let us take up a practical case and the directions which have been given for it.

The Evaluation of Solid Sodium Bicarbonate.—The procedure recommended by Lunge¹ is as follows:

"A 5 g. sample of bicarbonate, contained in a 1000 cc. beaker, is dissolved in about 100 cc. of distilled water, previously boiled out and cooled to 15° or 20°; the process of solution may be hastened by breaking up the large particles by means of a glass rod, but all stirring or violent motion of the liquid must be avoided. These precautions are absolutely necessary to the attainment of trustworthy results, since otherwise the bicarbonate solution loses carbonic acid very readily. The temperature of the water must be between 15° and 20°; for if it is colder dissolution is too slow, while if it is warmer the danger of loss of carbonic acid is greater. In this solution the double quantity (10 g.) of pure NaCl is now dissolved, the solution is cooled to nearly 0°; phenolphthalein is added and the buret containing the acid so arranged that its tip dips into the solution. It is now titrated with 1 *N* HCl until the red color has just disappeared (= *a* cc. acid); methyl orange is added and the titration continued until the color changes (= *b* cc. acid); 2*a* represents the Na₂CO₃, *b* — *a* the NaHCO₃."

The precautions emphasized by Lunge are in accordance with, and could have been predicted from, the principles discussed in this paper. Retention by the solution of all the CO₂, which is essential if reliable results are to be attained, is favored by low temperature and by the avoidance of any stirring, produced either by intention or by the dropping in of the acid during the titration. It is also essential that the change bicarbonate to carbonate, which will always tend to proceed unless the CO₂ pressure has the appropriate value (a condition which in practice is altogether exceptional) be slowed up as much as possible; this change, which is an ionic reaction according to the scheme $2\text{HCO}_3^- = \text{CO}_3^{2-} + \text{CO}_2 + \text{H}_2\text{O}$, can be slowed up by diminishing the concentration of HCO₃⁻ in the solution, and this is accomplished by the addition of a large amount of sodium chloride, which sets back the ionization of the carbonate. Lunge's interpretation of the end points is, as we have seen, not absolutely correct; nevertheless it is ample for the practical evaluation of sodium bicarbonate as carried out according to the above directions.

¹ G. Lunge, "*Chemisch-technische Untersuchungsmethoden*," 5te Auflage, I, p. 477.

V. Determination of Free Carbonic Acid in Solution.

The method most generally used appears to be that proposed first by Trillich (but also referred to as the Seyler¹ method); namely, to titrate with a freshly prepared solution of sodium carbonate (0.02 or 0.05 *N*) with phenolphthalein as indicator until a permanent pink color is developed. In practice it has been found² that certain precautions must be observed, and that in any case the method does not always yield accurate results; for instance, the result is generally too low unless the total concentration of carbonate present at the end point is small—a condition which implies that the aggregate equivalent concentration of free CO₂, carbonate and bicarbonate present in the liquid under investigation was below a certain limit. We shall now consider the theory underlying this method in order to elucidate the reason for this apparently anomalous behavior and to ascertain if it be possible to obviate these disadvantages.

In this titration the reaction is



or better, $\text{H}_2\text{CO}_3 + \text{CO}_3^{--} \rightleftharpoons 2\text{HCO}_3^-$.

It is, therefore, the equilibrium which forms the subject of this paper; and it is worth noting that, in the ordinary interpretation of the results of this method, there is the tacit assumption that this equilibrium adjusts itself practically instantaneously. The relation between the several concentrations at equilibrium is given by Equation IV, *viz.*,

$$[\text{HCO}_3^-]^2/[\text{CO}_3^{--}] = 7100[\text{H}_2\text{CO}_3] = 7100cP.$$

Now [H₂CO₃] is at equilibrium determined, in accordance with Equation I, by the partial pressure of CO₂ in the atmosphere in contact with the solution; and for a given total concentration of carbonate, as we have seen, both [HCO₃⁻] and [CO₃⁻⁻] are fixed if the alkalinity of the solution (*i. e.*, [H⁺] or [OH⁻]) is fixed, as it is in fact at the end point as registered by an indicator. But, as Equation IV shows, the two quantities [H⁺] and *P* are not independent variables; if we choose a value of *P*, we thereby fix [H⁺], provided that equilibrium obtains, and conversely. Consequently, unless the value of *P* prevailing at the time of titration corresponds to that of [H⁺] registered by the indicator, the end point will tend to be uncertain and the result of the titration incorrect; and it is obvious that these two quantities can have corresponding values only exceptionally, for, unless by the adoption of some special procedure to control *P*, its value in actual titrations is accidental and may vary from

¹ C. A. Seyler, *Chem. News*, 70, 104 (1894); *Analyst*, 22, 312 (1897).

² First, apparently, by Paul, Ohlmüller, Heise and Auerbach (*Arb. Gesundheitsamt*, 23, 333 (1906)); independently, since then, by several others. F. Guth (*Gesundheitsingenieur*, 31, 737 (1908)) gives a large number of references to the literature up to that time; he too observed that this method is not exact, but considered it good enough in practice.

one hour to another. An example may serve to bring out this point. When phenolphthalein just turns pink, $[H^+]$ the concentration of hydrogen ion in the solution is, according to the work of Rosenstein,¹ about 10^{-9} . Consequently if we conduct a titration with phenolphthalein, the conditions for equilibrium at the end point between $[HCO_3^-]$, $[CO_3^{2-}]$ and the partial pressure P of CO_2 in the air-space above the liquid are, from Equations V and VI $[HCO_3^-] = 12.6 P$, $[CO_3^{2-}] = 0.685 P$, whence $[B^+] = [HCO_3^-] + 2[CO_3^{2-}] = 14 P$. In other words, under the conditions specified, the total equivalent aggregate concentrations of carbonate and bicarbonate at the end point must for equilibrium be $14 P$, or about 14×0.0005 or 0.007 under laboratory conditions. If $[B^+]$ at the end point is less than 0.007 , CO_2 will tend to be absorbed continuously by the solution and thus to cause a repeated fading out of the color until the total alkali added reaches this limiting value; if $[B^+]$ is greater than 0.007 , the results will tend to be low, apart altogether from the circumstance that the solution will tend to lose CO_2 to the air space above it. Now it is obvious that the smaller this air space is, the less CO_2 must be transferred to bring the two phases into equilibrium and consequently the smaller the error; this is the theoretical basis for the procedure recommended by Tillmanns and Heublein,² namely, to titrate rapidly in a closed flask containing as little air-space as is compatible with the manipulations.

Now if the equivalent concentration of CO_2 , either free or combined, was such that at the end point $[B^+]$ is greater than the limiting value (the magnitude of which depends upon the H^+ concentration actually registered by the indicator) then some fraction of the free CO_2 will be "covered up"—an effect which has been noted by several investigators. But by a suitable choice of indicator one is enabled, in theory at least, to conduct the titration of any solution so that the error from this source shall not exceed a certain limit; the information required is given in Table II in conjunction with a table of indicator constants. As an example, if the untitrated CO_2 is to be less than 1 part per million, and the total concentration of base at the end point is 0.001 ,³ one must choose an indicator which changes when $[H^+]$ is between 10^{-8} and 10^{-9} —e. g., phenolphthalein

¹ Rosenstein, THIS JOURNAL, 34, 1117 (1912), *q. v.* The value of $[H^+]$ at the end point varies with the amount of indicator added, the concentration of salt present at the end point, and the depth of color fixed upon as denoting the end point.

² Tillmanns and Heublein, *Z. Nahr. Genussm.*, 20, 617 (1910). The apparent accuracy of the determinations of free CO_2 by titration recorded in this paper is due to the circumstance that the authors happened to choose the particular concentration of phenolphthalein which admits of correct results with solutions of the concentration which they investigated.

³ This implies that the free CO_2 originally present did not exceed $0.0005 N$ or about 22 parts per million, or a smaller amount if any carbonate was present originally in the solution.

used under appropriate conditions.¹ It is obvious, therefore, that the use of a single indicator under specified conditions cannot yield correct results in general; that with increasing concentration of either carbonate or indicator the amount of free CO_2 left untitrated increases rapidly. Similar conclusions have also been reached by Auerbach.²

These conclusions are in harmony with the careful experimental work of Noll,³ who made a large number of titrations of the free CO_2 in distilled water in various solutions of bicarbonates of sodium, calcium, and magnesium and in natural waters, using various concentrations of phenolphthalein, and compared the results with those of control experiments made by the Pettenkofer method. Table III illustrates his results; in each case he took 200 cc. of the solution, added 0.5 cc. of a solution of the given dilution of phenolphthalein in 96% alcohol, and titrated until a faint permanent pink color was obtained.

TABLE III.—THE VARIATION OF THE AMOUNT OF "FREE CO_2 ," AS ESTIMATED BY TITRATION WITH Na_2CO_3 SOLUTION, WITH THE AMOUNT OF INDICATOR; ACCORDING TO THE EXPERIMENTS OF NOLL.
"Free CO_2 " (mg. per l.).

Dilution of phenolphthalein solution. ⁴ 1 g. phth. to x g. 96% EtOH.	In Hamburg water stated to contain about 13.6 mg. CO_2 per l.	In 0.0112 N NaHCO_3 stated to contain about 11.7 mg. CO_2 per l.
2000	16.5	26.4
1500	14.85	...
1000	13.2	15.4
800	12.1	13.2
600	11.0	11.55
400	9.35	8.25
200	7.7	3.85
100	6.6	(very faint pink)
50	5.5	(faint pink)
30	3.85	(red)

Noll's conclusions follow:

"The determination of free carbonic acid in waters by the Trillich method yields reliable results if the waters contain no bicarbonate and if the content of free CO_2 is not so high that an appreciable concentration of bicarbonate is present at the end point. If on the other hand the waters contain any considerable amount of bicarbonate, the results will be incorrect unless the proper strength of phenolphthalein solution is chosen; the results for CO_2 may be too high as well as too low, since bicarbonate solutions which appear acid when tested by small amounts of indicator may appear to be alkaline when a larger concentration of indicator is used."

In a later paper⁵ Noll investigates the use of rosolic acid as an indi-

¹ For a discussion of this see Rosenstein, *THIS JOURNAL*, 34, 1117 (1912).

² Auerbach, *Z. angew. Chem.*, 25, 1722 (1912).

³ Noll, *Z. angew. Chem.*, 25, 998 (1912); see also Morgulis and Fuller, "Can Carbon Dioxide in Sea Water be Directly Determined by Titration," *J. Biol. Chem.*, 24, 31 (1916).

⁴ 0.5 cc. to 200 cc. liquid taken in each titration.

⁵ Noll, *Z. angew. Chem.*, 26, 85 (1913).

cator in this titration, and finds, in agreement with Tillmanns and Heublein,¹ that the results so obtained are incorrect; this could, indeed, be inferred from Table II and the known constant of this indicator. Indeed, as was pointed out above, while in any specified case one indicator may yield more nearly correct results than another, no indicator will be satisfactory over the whole range of concentrations; and the choice of a suitable indicator and of the proper end point can be made only if the total CO_2 content is known in advance. It has also been proposed to titrate with NaOH or $\text{Ca}(\text{OH})_2$; but the choice of end point is open to the same uncertainty, and the results are unreliable—a conclusion which has also been confirmed by experience. This method is obviously altogether inapplicable to waters which contain some free acid other than carbonic acid, *e. g.*, to waters carrying a salt, such as FeSO_4 , which is readily hydrolyzed.

Altogether, then, titration methods, as ordinarily carried out, are of very little use as a means of accurately determining small quantities of free CO_2 in solution; such a method might, perhaps, be used, by reason of its convenience and rapidity, in cases where it is necessary to make comparative determinations on a long series of very similar waters; but it would then be advisable to calibrate the method by applying it to known solutions, as has been suggested by Auerbach² and carried out very recently by Winkler.³

Free CO_2 in solution can be determined by boiling the liquid, or by aspirating a current of air through it, and absorbing the CO_2 set free by either means, but only if it exists entirely in uncombined form. If some of it exists in combined form, the results of such a procedure have no very definite meaning; for as the free CO_2 is removed, the equilibrium between HCO_3^- , CO_3^{--} and CO_2 tends to reestablish itself and more CO_2 is regenerated. Consequently the results will always be too high, and be higher the longer the boiling or aspiration process is continued; if the latter is conducted rapidly, the weight of CO_2 absorbed will be an approximate measure of the aggregate amount existing in the solution as free CO_2 and as bicarbonate. Indeed by aspirating a stream of air absolutely free from CO_2 through a carbonate solution for a long enough time, one can—theoretically at least—drive out absolutely all the carbonate, and be left with a solution containing only hydroxide. Similar remarks apply to the process of “raining” the solution (*i. e.*, letting it fall in small drops through the air), a procedure employed by Tillmanns and Heublein as a means of causing the solution to lose CO_2 rapidly. Obviously, therefore, it is not generally admissible to use this or an analogous procedure

¹ Tillmanns and Heublein, *Z. Nahr. Genussm.*, 20, 617 (1910).

² F. Auerbach, *Z. angew. Chem.*, 25, 1722 (1912).

³ L. W. Winkler, *Z. anal. Chem.*, 53, 746 (1914).

for this purpose, as Classen does,¹ unless very approximate results will suffice; indeed, in special cases the result may be absolutely erroneous. For instance, Hillebrand,² in analyzing a mineral water containing mainly the radicals SO_4 , Zn , Ca , CO_2 (in the order of their abundance), found that *all* the CO_2 was expelled on simply boiling the water, although it was neutral to litmus, and that simultaneously ZnO was precipitated; this loss of CO_2 , which must occur to some extent with several other metallic radicals, notably with iron and under certain circumstances with magnesium, is determined by the solubility-product constants of $\text{Zn}(\text{OH})_2$ and ZnCO_3 .³ Incidentally, a determination of total solids by evaporation would, as Hillebrand notes, involve a very serious error in addition to those usually encountered.

Forbes and Pratt⁴ made a comparison of this method with titration methods, and found that their aspiration method yielded higher results, which they believed to be correct; for practical work, however, they favored the Lunge, Trillich or Seyler method (*i. e.*, titration with a solution of Na_2CO_3) by reason of its convenience. But, as we have seen, neither of these methods is to be recommended where accuracy is desired; this matters the less because the information desired can be obtained in other ways.

If accurate results are required, they can be secured by employing the method described recently by Swanson and Hulett.⁵ The principle of this method is to introduce a given volume of the liquid into an evacuated vessel of known volume, to shake until equilibrium between the CO_2 in both phases has been attained,⁶ and then to determine the proportion of CO_2 in the vapor phase—a determination which is simple, rapid and accurate.⁷ By combining this result with the appropriate solubility of CO_2 we can derive directly the concentration of free CO_2 in the liquid as at the end of the experiment; whence by taking into account the relative

¹ Classen, "*Ausgewählte Methoden der Analytischen Chemie*," 2, 189 (1903).

² W. F. Hillebrand, *Am. J. Sci.*, 43, 418 (1892).

³ For the analogous case with magnesium see Johnston, *THIS JOURNAL*, 37, 2015 (1915).

⁴ F. B. Forbes and G. H. Pratt, "The Determination of Carbonic Acid in Drinking Water," *THIS JOURNAL*, 25, 742 (1903). These authors give many good practical hints, especially in connection with the method discussed in Section IV *supra*.

⁵ Swanson and Hulett, *THIS JOURNAL*, 37, 2490 (1915). The ideal method would be, as Swanson and Hulett point out, to prepare and know the composition of the gas phase which would be in equilibrium with the solution; but this would hardly be a practical analytical method.

⁶ If no appreciable amount of carbonate (as distinct from bicarbonate) is present after shaking, the attainment of this equilibrium would require only a few minutes; if otherwise, time must be allowed for the readjustment of the equilibrium between HCO_3^- , CO_3^{--} and CO_2 in solution, for the position of equilibrium is shifted by the loss of CO_2 to the vapor space.

⁷ J. Walker, *J. Chem. Soc.*, 77, 1110 (1900); cf. A. G. Woodman, *THIS JOURNAL*, 25, 150 (1903).

volumes of the liquid and vapor phase we can readily calculate the original concentration of free CO_2 , provided either that no appreciable proportion of CO_3^{--} was present at the end of the experiment or that the volume of the vapor phase was very small as compared with that of the liquid. In practice the latter condition would usually not be fulfilled, but the former would, since one would be unlikely to employ this method unless the amount of free CO_2 is considerable (and hence, CO_3^{--} small); yet with the above data and a knowledge of the amount of base equivalent to the combined CO_2 the calculation of the original proportions of carbonate, bicarbonate and free CO_2 can be performed in all cases, though it may be somewhat troublesome.¹

It must, of course, always be borne in mind that this analysis only tells us the quantity of free CO_2 present in the liquid at the time of analysis, a quantity which bears no necessary relation to the amount originally present, unless due precautions have been taken in collecting and preserving the sample. The same remark applies to all of the determinations discussed in this paper.

VI. Estimation of Total CO_2 , Free and Combined.

The best procedure appears to be that recommended and described fully by Treadwell.² The principle of this method is to expel the carbon dioxide first by reducing the pressure over the liquid and finally by adding acid and heating until the expulsion is complete; the volume of gas thus set free is read off. This method possesses two great advantages: that there is no doubt as to the interpretation of the results (which cannot be said of all the methods proposed); and that the determination may readily be made in a short time at the source of the water, so that errors due to loss of CO_2 are reduced to a minimum. Equally good results are also obtained by absorbing the expelled CO_2 in suitable tubes, and weighing it; the use of this method, which obviously can only be carried out in a laboratory, is indicated whenever the total amount of CO_2 is small.

Mention should also be made of the Winkler method,³ because it has been used extensively; he expels the CO_2 by generating hydrogen from zinc and hydrochloric acid within the solution, absorbs it in caustic potash and determines the increase in weight. But in a quite recent paper⁴ he himself notes that there are sources of error—namely, that the CO_2 is not completely expelled, and that some water passes over and is absorbed—

¹ The mode of calculation is analogous to that employed in computing the solubility of calcite in water for various partial pressures of CO_2 (see *THIS JOURNAL*, 37, 2011 (1915)).

² Treadwell, "Analytical Chemistry," 1st ed., Vol. 2, p. 309 (1906). It is a modification of the original Petterson method.

³ L. W. Winkler, *Z. anal. Chem.*, 42, 735 (1903).

⁴ *Ibid.*, 52, 421 (1913); cf. Casares and de Rubies, *C. A.*, 7, 3377 (1913).

to obviate which he recommends that the apparatus be calibrated by working with known similar solutions under the same conditions. But, apart from this disadvantage, this method is inconvenient in the field, and hence is not well adapted to the determination of the total CO_2 in natural waters. Titration methods have also been used, but they need not be discussed further here, for they are substantially identical with those already discussed.

VII. General Conclusions.

In the foregoing pages we have reviewed the most important methods for the determination of the various constituents of a solution containing alkali carbonates; some of these methods yield accurate results, while others do not. If due precautions are taken, accurate determinations of the total base equivalent to the combined CO_2 and of the *total* CO_2 are readily made; but the results of all estimations of the amount of free CO_2 , of bicarbonate (half-bound CO_2), or of carbonate (bound CO_2) must be scrutinized carefully, as they may be very much in error. The reasons for this are in the main two: (1) That in such solutions there is equilibrium between CO_2 (which in turn is determined by the proportion of CO_2 in the air), HCO_3^- and CO_3^{2-} and the base B^+ , the state of which is altered—and altered fairly rapidly—by any change in the concentration of any of these constituents; consequently any attempt to estimate the proportion of one of these constituents cannot prove successful unless it is practicable to slow up the readjustment of this equilibrium to such an extent that the change in concentration of the constituent during the time required for the analysis is inappreciable; (2) that a comparatively slight change in the concentration of hydrogen ion corresponds to a much larger change in the concentrations of CO_2 free and combined, and that the concentration of H^+ at the *proper* end point of the titration (*i. e.*, for correct results) is not an invariable quantity, but depends upon the constitution of the solution being analyzed; consequently the result obtained depends in a marked degree upon the indicator adopted and upon the end point chosen. Indeed, as we have seen, no single indicator and no arbitrary end point can yield satisfactory results over the whole range of possible concentrations.

The least satisfactory method in general is the titration method for free CO_2 as ordinarily carried out, for the results cannot be interpreted unless the constitution of the solution is already known. This method might, of course, yield satisfactory comparative—though somewhat empirical—results when applied to a long series of very similar waters, as in the daily testing of a water supply. The free CO_2 is readily determined by a gasometric method, provided that the concentration of combined CO_2 is very small; if it should prove necessary to determine free CO_2 directly in a solution containing a material amount of combined

CO₂, one can achieve any desired accuracy in the result by observing the precautions discussed in the text. The most common method of estimating the relative proportions of bicarbonate and carbonate—*viz.*, to titrate first with phenolphthalein, subsequently with methyl orange—also yields only approximate results; these amounts can, however, be determined with sufficient accuracy in many cases by following the procedure recommended by Küster and discussed in the text.

On the other hand it is doubtful if it is worth while making the latter determinations, especially in natural waters, for the following reasons: In the first place, we are dealing with an equilibrium capable of fairly rapid readjustment, and so any change in the proportion of one constituent affects—in many cases, very markedly—the proportions of the others; consequently any method, even if it is in itself reliable, will not yield information as to the true proportions originally present in the solution unless due precautions are observed to prevent any alteration in the solution previous to the analysis—and that such precautions have in many cases not been taken is evident if one glances at any collection of water analyses. In the second place, since we are dealing with an equilibrium, there is no point in actually determining all of these constituents, because if we determine a certain number of them, we can calculate the concentration of each of the others; in other words, we can obtain just as much useful information—*i. e.*, information which we can interpret—from this smaller number of determinations. For we are justified in inferring that natural waters have had time to attain substantial equilibrium in respect to these components under the prevailing conditions. This, of course, does not imply that they are necessarily in equilibrium in a water as it issues from a spring, for such water is encountering rapidly changing conditions; on the other hand it is hard to see what useful conclusions we can draw from determinations of the concentration of, for instance, carbonate or bicarbonate present under such circumstances.

In general, then, it suffices to determine (a) the total base equivalent to the combined carbonate, (b) the total CO₂, free and combined, both of which are easy, reliable and unaffected by the presence of alkaline earths or of iron; for with a knowledge of these one is enabled to calculate the concentration of (c) carbonate, (d) bicarbonate, (e) hydrogen ion, which is a measure of the degree of acidity (or alkalinity) of the water. Alternatively one may in certain cases prefer, instead of (b), to determine either the proportion of bicarbonate to carbonate—a determination which can, subject to certain conditions, be made accurately—or the alkalinity directly by means of indicators in conjunction with a series of comparison solutions; for, when the respective ionizations (which depend upon the concentration of total base, [B⁺]) are taken into account, these two quantities are related to one another by Equation III or IIIa and to

the other quantities by the other appropriate equations. Which procedure one chooses depends upon individual preferences as regards manipulation and computation, and upon what one is chiefly interested in ascertaining; which brings up the question as to which of these several quantities has the greatest practical utility in each case. But it is to be observed that for all scientific, as well as for many technical purposes, we wish to know the equilibrium, so we would choose the most convenient and most accurate way under the circumstances of ascertaining the concentrations of the factors.

Let us consider, for example, the suitability of a water for use in a boiler, insofar as it is affected by the presence of CO_2 combined and free. For the sake of simplicity we shall suppose that the only base combined with the carbonic acid is lime. The total amount of calcium carbonate present is limited¹ by the total concentration of CO_2 ; though it need not correspond quantitatively to the latter—in other words, the water may not be saturated with respect to calcium carbonate, in which case a definite proportion of the free CO_2 will be “aggressive,” a question to which we shall revert presently. However this may be, the CO_2 will be expelled very soon after the water enters the boiler, and we shall have in the boiler a saturated solution which deposits CaCO_3 as the water is evaporated. This precipitation within the boiler can be minimized by reducing the content of carbonate before the water enters the boiler; this can be accomplished by blowing air through the water and adding an amount of alkali² (soda or slaked lime) equivalent to the bicarbonate present *at the time of addition*. This amount has usually been taken to be equivalent to the difference between the phenolphthalein and methyl orange end points; but this is, as we have seen, a somewhat uncertain procedure which tends to lead one to add more alkali than is requisite, and any excess of alkali is undesirable because it leads to foaming within the boiler. Consequently one should determine the concentration of bicarbonate by the accurate method, or at least calibrate by means of this method the procedure which is employed. The final amount of calcium carbonate will always correspond to its solubility under ordinary atmospheric conditions, *i. e.*, about 60 parts per million; it will not be diminished substantially by any permissible residual concentration of alkali, but can be materially decreased if the precipitation is carried out at elevated tempera-

¹ In presence of calcium sulfate it will of course always be smaller by an amount readily calculable; but this we are not taking into consideration here.

² Calcium sulfate is got rid of by the addition of the equivalent quantity of Na_2CO_3 . The equilibrium $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightleftharpoons \text{Na}_2\text{SO}_4 + \text{CaCO}_3$ proceeds further to the right (1) the greater the solubility of CaSO_4 (2) the smaller the solubility of CaCO_3 ; consequently the process should be carried out so far as practicable at a low temperature and after the CO_2 has been removed.

ture, since both the solubility of CO_2 and the solubility-product constant of CaCO_3 decrease with increase of temperature.

Let us now take up the case of a water which contains CO_2 in excess of the amount required to keep all the lime in solution. It had been observed that certain waters attack concrete, dissolving out CaCO_3 , or iron pipes and by doing so cause trouble in the water supply;¹ this was attributed to what was called the "aggressive" CO_2 , which by many was assumed to be identical with the total free CO_2 . But when the endeavor was made to prevent this action by removing all of the free CO_2 , other difficulties were encountered which remained unaccountable until in 1912, Tillmanns and Heublein, having learned that the solubility of CaCO_3 depends upon the partial pressure of CO_2 in the adjacent air, deduced that the "aggressive" CO_2 was that amount of the free CO_2 in excess of what was required to keep the CaCO_3 (or other insoluble carbonate) in solution. Accordingly, they made up a series of solutions containing CaCO_3 and free CO_2 , left them in contact with pieces of marble for 10 days or more, and finally determined the concentrations of bound and free CO_2 ; in effect, therefore, they made determinations of the solubility of CaCO_3 in water containing various proportions of CO_2 . The results when plotted are in general agreement with those of Schloesing, though, since the temperature of experiment is indefinite, it is useless to calculate any definite constant from them; this was, indeed, done roughly by Auerbach² who gave a better smoothed out curve, and a simple geometrical construction, by means of which the concentration of "aggressive" CO_2 may be read by inspection from the solubility curve. This amount can also be calculated readily from the equations given in a previous paper,³ if lime is substantially the only base present; otherwise, since the solubility-product constants of the various carbonates are different, these curves and equations are not applicable, and it would be better to determine directly by experiment the concentration of aggressive CO_2 . This concentration cannot be ascertained from experiments with any indicator, because the degree of alkalinity at which we begin to have aggressive CO_2 is not an invariant quantity—in other words, the alkalinity of saturated solutions of carbonates is not constant, but depends upon the total base in solution. If now, in an attempt to remove this aggressive CO_2 (by blowing air through the water, or otherwise) too much CO_2 is removed we are left with a super-saturated solution of carbonates which will slowly be deposited—a process which reproduces free CO_2 which again can act aggressively and cause trouble. Similar remarks apply to the process for the removal of iron by

¹ References are given by Tillmanns and Heublein, *Gesundheitsingenieur*, 35, 669 (1912); also by Tillmanns, *J. Gasbeleuchtung*, 56, 370 (1913).

² Auerbach, *Gesundheitsingenieur*, 35, 809 (1912).

³ J. Johnston, *THIS JOURNAL*, 37, 2011 (1915).

blowing air through the water; and the redissolving of iron by treated water has been an occasional source of trouble.¹

These instances have been discussed at some length because they illustrate the point that by considering that there is a mobile equilibrium and applying the appropriate quantitative relations we are enabled to coördinate and account very readily for things which otherwise are isolated and inexplicable facts. The application of these principles to other specific cases may be made in the same way, though in some cases experimental work on the constants involved may be required before the complete quantitative solution of the problem can be given.

Summary.

Within any solution containing carbonate there is a readily attained equilibrium between the carbonate ion CO_3^{--} , the bicarbonate ion HCO_3^- , and the carbonic acid H_2CO_3 , and in turn between the carbonic acid and the partial pressure of carbon dioxide above the solution; consequently these molecular species can coëxist only in definite proportions determined by the several equilibrium constants. An examination from this standpoint of the most commonly used titration methods for the estimation of the combined and free CO_2 in solution leads to the conclusion that many of these procedures do not yield definite results—a conclusion which is corroborated by all of the careful comparative experimental work bearing on these methods. In principle the only absolutely reliable methods are those for the total base combined with the carbonic acid and for the *total* CO_2 present in solution; in practice they yield accurate results provided that due attention is paid to the conditions discussed, or referred to, in the paper. But these two determinations suffice in general to characterize the solution with respect to either its content of free CO_2 , the proportion of carbonate to bicarbonate, or the degree of alkalinity or acidity; for, since we are dealing with an equilibrium capable of fairly rapid readjustment, we are justified in applying the equilibrium constants to calculate the above quantities in the great majority of those cases in which a knowledge of them is of real importance.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON.]

THE COMPLETE SOLUBILITY CURVE OF CALCIUM CARBONATE.

BY JOHN JOHNSTON AND E. D. WILLIAMSON.
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Since the publication of a previous paper² dealing with the solubility-

¹ For references see Tillmanns and Heublein, *Gesundheitsingenieur*, 35, 609 (1912); or Tillmanns, *J. Gasbeleuchtung*, 56, 370 (1913).

² Johnston, *THIS JOURNAL*, 37, 2001 (1915), q. v.; hereinafter referred to as *Loc. cit.*

product constant of calcium and magnesium carbonates, several additional points have come up which deserve consideration. These points are, moreover, of some general importance since they apply, *mutatis mutandis*, to any carbonate (or indeed to salts of any dibasic acid); they are elucidated immediately by the consideration of the complete solubility curve of the carbonate at any temperature. We shall, therefore, discuss briefly the relation between the partial pressure of CO_2 in equilibrium with the solution and the total concentration of base in equilibrium with the stable solid phase; the latter will be hydroxide, carbonate or bicarbonate¹ according to conditions, as a carbonate is stable in presence of its aqueous solution only between certain limits of pressure of CO_2 , these limits being fixed for a given base at a given temperature.

We begin by considering the equilibrium between the hydroxide $\text{M}(\text{OH})_2$ and the aqueous solution saturated with it as affected by a progressive increase from zero of the partial pressure P of CO_2 in the atmosphere in contact with the solution. Addition of CO_2 is followed by a distribution between the vapor and liquid phases until there is equilibrium between the residual partial pressure of CO_2 and the H_2CO_3 in solution, and in turn between the latter and the several ions; the net effect of this is a definite decrease in $[\text{OH}^-]$, the concentration of hydroxide ion, which necessitates that more of the hydroxide dissolve in order to keep the solubility-product $[\text{M}^{++}][\text{OH}^-]^2$ constant. Consequently the total concentration of M^{++} increases, part of it being now associated with carbonate and bicarbonate; in other words, the apparent solubility of the base increases if the method of analysis of the solution is a determination of M , whereas it would decrease if one should determine $[\text{OH}^-]$.² This process continues until the product $[\text{M}^{++}][\text{CO}_3^{--}]$ reaches the value requisite for the precipitation of MCO_3 (on the assumption that supersaturation does not occur) which, for a given base, takes place at a definite value of P which depends only upon the temperature; this transition pressure P_1 is, at a given temperature, the highest under which solid hydroxide is stable and the lowest at which solid carbonate is stable.

At P_1 the solubility (as measured by the total $[\text{M}]$) begins to diminish,³ because increase of P increases $[\text{CO}_3^{--}]$ while the product $[\text{M}^{++}][\text{CO}_3^{--}]$ must remain constant so long as MCO_3 is the stable solid phase; this increase of $[\text{CO}_3^{--}]$ continues until a definite pressure P_0 is reached, when the formation of bicarbonate in the solution becomes the predominant

¹ Throughout this paper we presume that no basic carbonate exists as a stable solid phase.

² Manifestly one could not determine $[\text{OH}^-]$ by an ordinary titration method, but would have to use some method which does not alter the equilibrium.

³ This descending portion of the curve will not be realizable if the hydroxide is stable beyond a certain limiting value of P , *vis.*, P_0 (*cf. postea*) which varies very little from one base to another.

reaction and $[\text{CO}_3^{--}]$ begins to decrease again. P_0 is thus a minimum in the solubility curve. With further increase beyond P_0 the concentration of both M^{++} and HCO_3^- increases steadily until the precipitation value of the product $[\text{M}^{++}][\text{HCO}_3^-]^2$ is reached at P_1 , which is a transition pressure at which both carbonate and bicarbonate are present as stable solid phases. Beyond P_1 bicarbonate alone is stable, and its total solubility falls off very slowly with further increase of partial pressure of CO_2 .

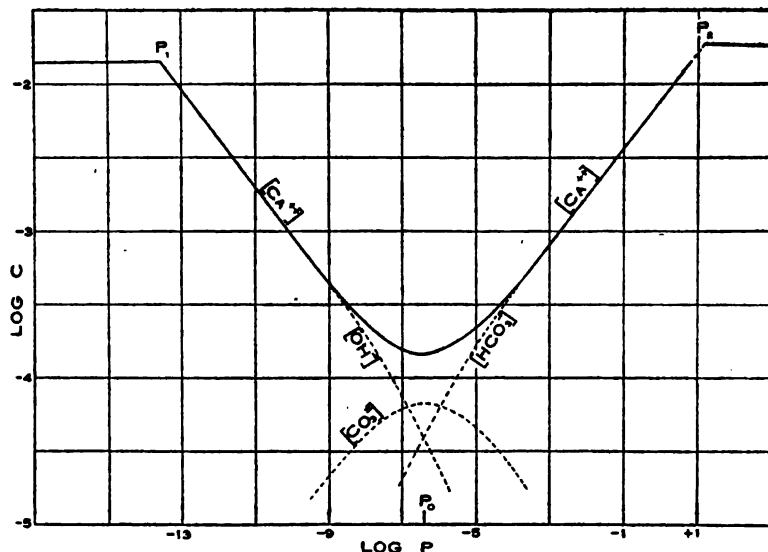


Fig. 1.—Graph of $\log C$ (C = ionic concentration) against $\log P$ (P = CO_2 pressure in atm.) for the several ions in the system $\text{CaO-H}_2\text{O-CO}_2$ at 16° . The stable solid phase to the left of P_1 is hydroxide, between P_1 and P_2 is carbonate, and to the right of P_2 bicarbonate. The several dotted curves are the solubility curves which would be obtained if the concentration of one or another of these ions were determined by analysis; the full curve, if correction is made for incomplete ionization, represents the solubility as ordinarily determined by estimation of calcium.

These relations are obvious from Fig. 1, which shows the variation with P of the total concentration¹ of Ca^{++} (which if it were corrected for the incomplete ionization, would be the solubility of the solid, as ordinarily measured), and also of $[\text{OH}^-]$, $[\text{CO}_3^{--}]$ and $[\text{HCO}_3^-]$; obviously $2[\text{Ca}^{++}] = [\text{OH}^-] + 2[\text{CO}_3^{--}] + [\text{HCO}_3^-]$. These curves were constructed on the basis of the equilibrium equations discussed in what follows; the only assumption made is that each solubility-product remains constant throughout the range in which the particular solid phase

¹ The scales had to be made logarithmic, as otherwise the left hand portion of the diagram up to P_0 would have been too small to be visible; for some numerical data see Table I.

is stable. The figure shows very strikingly to what different results we might be led if, instead of determining by experiment the total concentration of M , we were to analyze for one of the other three molecular species; such a course would be unlikely in the case of the carbonates but might be followed in other analogous cases, *e. g.*, sulfites or sulfides. It may be remarked, moreover, that it is entirely possible that the range P_1P_2 within which the normal carbonate is the stable solid phase may in certain cases be very small, or even zero; the main conditions for this would be that the hydroxide be relatively insoluble and the bicarbonate not too soluble.

The Value of P_0 .—The minimum solubility is realizable only if carbonate is the stable solid phase at the pressure P_0 , *i. e.*, only if P_1 is less than P_0 . The equations¹ giving the necessary relations are as follows, the symbols being the same as before with the addition of m , the valence of M under these conditions, the ion-concentration of M being indicated by $[M]$:

$$[M]^{2/m} [\text{CO}_3^{--}] = K_C \quad (\text{I})$$

$$[\text{HCO}_3^-] = r[\text{H}_2\text{CO}_3] [\text{CO}_3^{--}] \quad (\text{VI})$$

$$[\text{OH}^-] = K_W^2 [\text{CO}_3^{--}] / k_1 k_2 [\text{H}_2\text{CO}_3] \quad (\text{X}')$$

These combined with the condition

$$m[M] = [\text{HCO}_3^-] + 2[\text{CO}_3^{--}] + [\text{OH}^-]$$

yield the expression

$$m[M] = \sqrt{\frac{K_C r [\text{H}_2\text{CO}_3]}{[M]^{2/m}}} + \frac{K_C}{2[M]^{2/m}} + \sqrt{\frac{K_C K_W^2}{k_1 k_2 [\text{H}_2\text{CO}_3] [M]^{2/m}}} \quad (\text{XIII})$$

as the equation of the curve representing the change of solubility of the carbonate with the concentration $[\text{H}_2\text{CO}_3]$, hence with P . Whence, by differentiating and substituting, we get

$$\frac{d[M]}{d[\text{H}_2\text{CO}_3]} = \frac{m[M] \{ [\text{HCO}_3^-] - [\text{OH}^-] \}}{2[\text{H}_2\text{CO}_3] \{ m^2 + m[M] + 2[\text{CO}_3^{--}] \}} \quad (\text{XIV})$$

which vanishes when $[\text{HCO}_3^-] = [\text{OH}^-]$; at this point $[\text{H}_2\text{CO}_3] = K_W/k_1$, wherefore, $cP_0 = K_W/nk_1$.

The order of magnitude of P_0 is, therefore, independent of what M is, though its value is not absolutely the same for the several carbonates because the appropriate value of c (absorption coefficient of CO_2) varies slightly from one saturated solution to another. At 18° , P_0 is (for calcite) 4.0×10^{-7} , a pressure which therefore is easily realizable, since it is only about the one-hundredth part of the proportion normally present in the atmosphere.

The Value of P_1 and P_2 .—These are obtained directly by combination of the appropriate solubility-product constants of carbonate (K_C),

¹ See *Loc. cit.*, p. 2011; Equation X' follows directly from combination of X and V.

hydroxide (K_H) and bicarbonate (K_B) with equations already given; the values follow:

$$P_1 = \frac{K_C}{K_H} \cdot \frac{K_W^2}{cnk_1k_2}$$

$$P_2 = \frac{K_B}{K_C} \cdot \frac{k_2}{cnk_1}$$

Equation XIII represents the solubility curve only between P_1 and P_2 ; similar equations are easily set up for the other two branches of the complete curve, *i. e.*, for the solubility of hydroxide and bicarbonate, respectively. Obviously, too, in case P_1 is greater than P_0 there will be no minimum on the solubility curve of the carbonate; this is so in the system $\text{MgO}-\text{CO}_2-\text{H}_2\text{O}$,¹ in which case P_1 is about 0.00037.

The Data for Calcium Carbonate.—In order to bring out certain points we have calculated² the solubility of CaCO_3 for a series of partial pressures extending from ordinary conditions downwards; and present the results in Table I, which supplements Table IV of the previous paper.

From the table it follows that at $16^\circ P_0$, the value of P at which there is the minimum concentration of calcium in solution, is 3.73×10^{-7} atm., corresponding to a solubility of about 16 mg. CaCO_3 per liter; on either side the solubility increases owing to the formation in solution of hydroxide on the one hand and of bicarbonate on the other. It is to be observed, moreover, that even at this minimum (which is the maximum concentration of CO_3^{--}) only about 46% of the Ca^{++} present is associated with carbonate, the remaining 54% being equally divided between hydroxide and bicarbonate; and that, except at pressures close to P_0 , the proportion of Ca^{++} associated with CO_3^{--} is very small. This

¹ See *Loc. cit.*, p. 2015. In Table VIII (p. 2016) the values of $[\text{CO}_3^{--}]$ in the fourth column are, through a printer's error, one-tenth of what they ought to be.

² For the method and the values of the constants used, see *Loc. cit.*, p. 2011. Since the publication of the previous paper, we have seen in manuscript a paper by Seyler and Lloyd (which is in course of publication in the *J. Chem. Soc. London*) in which they show that Na_2CO_3 is in all probability ionized to a much smaller extent than has generally been assumed; and that on this basis recalculation of McCoy's results, as well as of a series of experiments of their own, yields a value for nk_1/k_2 of about 7100 at 25° . The adoption of this value would lower the solubility-product constant K_C in the ratio of 56 to 71, and produce a corresponding change in the other calculated values; but for the present we have preferred to retain the previous value, for the following reasons: (a) Auerbach and Pick, in calculating k_2 from their work, assumed a degree of ionization of Na_2CO_3 comparable to that indicated by the work of Seyler and Lloyd, and obtained the value 6×10^{-11} at 18° ; whence nk_1/k_2 is 5100 at 18° , a temperature close to that we are considering (16°); (b) some of the other data are likewise uncertain; (c) in view of which, we preferred to keep the data consistent with those of the previous paper. In any case such changes will not alter the shape of the curve, but merely affect the absolute values, and to an extent which is hardly significant in the present state of accuracy of the experimental work which we are considering.

TABLE I.—THE CALCULATED ION-CONCENTRATIONS AND SOLUBILITY OF CALCITE IN WATER AT 16° IN CONTACT WITH AIR CONTAINING THE PARTIAL PRESSURE P OF CO_2 .

P^1	$[\text{HCO}_3^-] \times 10^4$	$[\text{OH}^-] \times 10^4$	$[\text{CO}_3^{--}] \times 10^4$	$[\text{Ca}^{++}] \times 10^4$	Parts CaCO_3 per million. ²
2.15×10^{-4}	10.0	0.0174	0.188	5.197	56
7.63×10^{-5}	7.0	0.034	0.260	3.777	40
7.62×10^{-5}	3.0	0.147	0.478	2.051	22
6.07×10^{-7}	1.0	0.614	0.666	1.473	16.0
3.85×10^{-7}	0.80	0.774	0.672	1.459	15.9
3.73×10^{-7}	0.787	0.787	0.672	1.459	15.9
2.19×10^{-7}	0.60	1.02	0.665	1.476	16.0
6.14×10^{-8}	0.30	1.82	0.593	1.654	18
9.78×10^{-9}	0.10	3.82	0.414	2.377	26
2.80×10^{-10}	0.01	13.3	0.144	6.81	74
3.16×10^{-14}	0.000235	277.0	0.0071	138.5	2000

table enables us to define the equilibrium when CaCO_3 is shaken up in a closed vessel completely filled with *pure* water; for in such a case $[\text{OH}^-]$ and $[\text{HCO}_3^-]$ must be very nearly equal, the small difference between them being merely the amount of CO_2 required to bring the solution into equilibrium with a virtual pressure somewhat *less* than 3.73×10^{-7} . Under such conditions, therefore, the solubility of CaCO_3 would be about 16 parts per million at 16°; nor would, as a consideration of the matter shows, the result be appreciably different though 99% of the volume of the vessel were occupied by pure air. Now Kendall³ in certain of his experiments used a method which approximately satisfies the above conditions, and found a solubility of 14 parts per million at 25°; in this connection we may remark that Kendall's results would have been very much higher if his air and water had been *completely* free from CO_2 .

The transition pressure P_2 between calcium carbonate and bicarbonate has been determined by McCoy and Smith⁴ to be about 15 atm. at 25°, bicarbonate being the stable solid phase above this pressure; the value of P_2 at 16° is not known, but is certainly of the same order of magnitude.

The transition pressure P_1 at which both hydroxide and carbonate

¹ From the equations it follows that $P = \frac{0.5b^3 + \sqrt{1.809b^3 + 3.927b^4 + 0.25b^5}}{4.85 \times 10^8}$

where $b = [\text{HCO}_3^-] \times 10^4$; when b and P are fixed, the other quantities are readily calculated.

² Calculated on the basis that the degree of ionization is about 0.92 throughout, except for the (approximate) value in the lowest row.

³ J. Kendall, *Phil. Mag.*, 23, 958 (1912).

⁴ McCoy and Smith, *THIS JOURNAL*, 33, 468 (1911). This important paper was inadvertently overlooked during the preparation of the previous paper. We are obliged to Dr. McCoy for directing our attention to it. They calculate K_C to be 0.93×10^{-3} at 25°, a value which agrees very well with that given in Table II *postea*.

are stable, can be calculated if we know the solubility-product constant (K_H) of $\text{Ca}(\text{OH})_2$. As far as one can judge from the somewhat discordant data available, the solubility of $\text{Ca}(\text{OH})_2$ at 16° is about 0.021 mols per liter; whence, on the basis that its degree of ionization in the saturated solution is about 70%,

$K_H = [\text{Ca}^{++}][\text{OH}^-]^2 = (0.015)(0.03) = 1.3 \times 10^{-6}$ at 16° and

$$P_1 = \frac{1.0 \times 10^{-8}}{1.3 \times 10^{-6}} \times 3.4 \times 10^{-11} = 2.6 \times 10^{-14}.$$

Consequently $\text{Ca}(\text{OH})_2$ can be the *stable* solid phase only when the partial pressure of CO_2 is extremely small, so small that such freedom from CO_2 could be realized only by means of extraordinary precautions; this fact may be correlated with the lack of satisfactory concordance of the data on the solubility of $\text{Ca}(\text{OH})_2$.

P_1 , however, can also be calculated in a totally different way, from independent data. P_1 is the pressure of CO_2 in equilibrium with solid hydroxide and solid carbonate in the solution saturated with respect to both at the particular temperature T , and, is therefore, a measure of the free energy change C accompanying the reaction III below; but the latter quantity is the difference¹ between the corresponding quantities A and B for the reactions I and II:



Now it was shown in a previous paper² that the dissociation pressure p (expressed in mm. Hg) is reproduced over the experimental range³ ($T = 850 - 1150$) by the formula

$$\log p = -9340/T + 1.1 \log T - 0.0012 T + 8.882$$

whence by extrapolation down to 289° abs. (i. e., 16°)

$$\log P_{289} = -23.97 \text{ (when } P \text{ is the pressure in atm.)}$$

and

$$A = \Delta F_{289} = -RT \ln P_{289} = 289 \times 4.576 \times 23.97 = 31700.$$

In an earlier paper⁴ it was shown that the free energy change of the re-

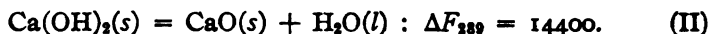
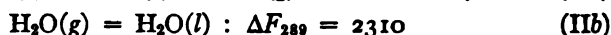
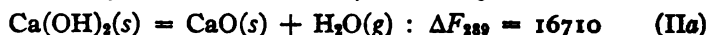
¹ We neglect here the small quantity corresponding to the difference between the vapor pressure of pure water and that of the water in the solution saturated with hydroxide and carbonate.

² J. Johnston, *THIS JOURNAL*, 32, 938 (1910).

³ Quite recently it was shown by Sosman, Hostetter and Merwin (*J. Wash. Acad.*, 5, 563 (1915)) that the pressure of CO_2 in equilibrium with CaCO_3 at 400° is of the same order of magnitude (0.002 mm.) as is indicated by the formula above.

⁴ J. Johnston, *THIS JOURNAL*, 30, 1359 (1908).

action IIa is $\Delta F = 25870 - 31.67T$, hence $\Delta F_{289} = 16710$; while that of reaction IIb at 289° is $= -RT \ln 0.0178^1 = -2310$.



Thus we calculate that C, the free energy change of reaction III, is $31700 - 14400 = 17300$ and hence

$$\log P_1 = -\frac{17300}{289 \times 4.576} = -13.08$$

so that $P_1 = 8.3 \times 10^{-14}$.

The agreement between this value and that derived directly from the solubility data is remarkable, especially in view of the uncertainty attaching to some of the factors involved in the calculation; the large extrapolation, for example, will be accurate only when the specific heats of the several solid substances shall have been determined throughout the temperature range. From this value of P_1 we may calculate backwards and find $K_H = \frac{K_C \times 3.435 \times 10^{-11}}{8.3 \times 10^{-14}} = 4 \times 10^{-6}$, as compared

with 13×10^{-6} derived directly; this latter value, it may be observed, is in all probability too high, since in its derivation it was tacitly assumed that no intermediate ions are formed, that the ionization proceeds solely according to the scheme $\text{Ca(OH)}_2 \rightarrow \text{Ca}^{++} + 2(\text{OH}^-)$. This substantial agreement between such different lines of evidence is important as a demonstration of the essential correctness of the views here discussed; it serves, moreover, either to increase confidence in the experimental data or else as a clue, by means of which errors may be more readily discovered.

TABLE II.—THE SOLUBILITY-PRODUCT CONSTANT OF CALCITE AT SEVERAL TEMPERATURES.

Temperature <i>t</i> .	Parts CaCO_3 per million. ($P = 0.00032$.)	<i>c</i> .	$K'C \times 10^6$.
0	81	0.0765	1.22
5	75	0637	1.14
10	70	0535	1.06
15	65	0455	0.99
20	60	0392	0.93
25	56	0338	0.87
30	52	0297	0.81

As regards the change of solubility of calcite with temperature, Wells² has made a series of determinations at temperatures between 0° and 30° , the solution being in contact with air containing 3.2 parts CO_2 per

¹ The vapor pressure, expressed in atm., of water at 16° .

² R. C. Wells, *J. Wash. Acad. Sci.*, 5, 617 (1915).

10,000; the results as interpolated from his curve are given in Table II, along with the appropriate values of $c (= \alpha/22.4$, where α is the absorption coefficient) and of the solubility-product calculated on the basis that nk_1/k_2 is 5600.

K'_C is given by the expression $\log K'_C = \bar{8}.087 - 0.006 t$; whence one can, using 5600 as the value of nk_1/k_2 , calculate the solubility of calcite for any partial pressure of CO_2 at any temperature up to 30° .

Summary.

The graph showing the concentration of calcium in the solution at equilibrium in the system $\text{CaO-H}_2\text{O-CO}_2$ is made up of three curves, along which the stable solid phase is hydroxide, carbonate, bicarbonate, respectively. The first extends only up to values of P , the partial pressure of CO_2 , of about 10^{-14} at 16° ; the second, starting from the transition point, decreases to a minimum and then rises again, as the value of P increases continuously, until P is about 15 atm.; beyond the second transition point bicarbonate is the stable solid phase. Along the whole course of the graph, all three ions OH^- , CO_3^{--} , HCO_3^- are present at relative concentrations depending upon P ; so in this, as in other analogous cases, the solubility curve ascertained by experiment would have different forms according as one determined one or other of the several molecular species in solution. Thus the maximum concentration of CO_3^{--} occurs when the solubility—as measured by the concentration of calcium in solution—is a minimum; and it is only within a restricted range of P that the base associated with CO_3^{--} is more than a fractional proportion of the total base in solution.

The transition pressure at which both hydroxide and carbonate are stable, may be calculated either from the solubilities of hydroxide and carbonate or from their thermal dissociation pressures; these two absolutely independent methods yield results surprisingly concordant, a circumstance which demonstrates the essential correctness of the views discussed in this paper.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

SUGGESTION CONCERNING THE STATEMENT OF THE PHASE RULE.

BY THEODORE W. RICHARDS.

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The most serious difficulty of the Phase Rule for beginners lies in the definition of the word "component," of which many varying definitions have been given by various authorities. Of these most are entirely legitimate, although they may lead to different choices as to the number of

components in special cases.¹ The difficulty lies in the fact that the restrictions imposed often cause the number of "components" to be different from the number of individual chemical substances taking part in the reaction.

No attempt will be made here to give all the varying definitions or explain the limitations which must be imposed upon them. The object of this note is to advocate briefly a different method of treatment, perhaps more generally acceptable to chemists and more easily comprehensible by beginners than most of the others. Doubtless it has been used before, but it does not seem to have been clearly stated or commonly recognized. The idea is this: instead of stating the Phase Rule in a very simple equation and placing all the burden of incomprehensibility upon the component, this method abandons the complex older idea of the component and substitutes another, that of the chemical "individual," or "constituent" which is easily understood by the chemist, and places all the necessary restrictions in definite form in a somewhat more complex but easily comprehensible equation defining the Phase Rule.²

According to this plan, the definition of the chemical "individual" is as follows: *The INDIVIDUALS of any reacting system are the separate chemical substances, UNDECOMPOSED IN THE REACTIONS CONCERNED, which are necessary to construct the system. The number of such individuals to be chosen is the smallest number necessary to construct the system.*

¹ See for example "The Phase Rule" by Alex. Findlay, p. 12 (London, 1904).

² Except for the fact that in most minds conversant with the subject the term "component" indissolubly involves restrictions, it would be better to retain this old term, giving it the new and simpler meaning. Professor Lash Miller convinced me that on this account the change of meaning is undesirable. The word "individual," however (suggested in conversation by Professor A. B. Lamb) seems to answer the requirement. The word "constituent" would be almost as good, but not quite so definite and distinctive. This, then, might be used; indeed it has already been used in a sense not very different from the present by Trevor (*J. Phys. Chem.*, 1, 22 (1896)); but his use of the word was somewhat freer than that needed here, as was also Bancroft's ("The Phase Rule," p. 227 (1897)). The qualification given above "undecomposed in the reactions concerned" is a very important one for the present purpose, although it does not appear in the earlier definitions; according to Bancroft's application, n , would sometimes be a minus quantity (p. 230, "The Phase Rule"—a suggestive book which did much to promote study of the subject). The interesting very recent treatment of Washburn ("Principles of Physical Chemistry, N. Y., 1915") is yet different, involving another idea called the "composition-number," although of course the fundamental idea is the same, as indeed it must be in any sound treatment of the Phase Rule. This present method of statement adopted above makes no attempt to define the kinetic mechanism needful for achieving the result. It records simply the facts, and may be made subject to any interpretation applicable according to any other formulation which likewise expresses the facts. Reference may be made to the interesting papers of Wegscheider (*Z. phys. Chem.*, 43, 89 (1903); 45, 496 (1903); 50, 357 (1904); 52, 171 (1905)).

If we define the individuals in this simple and reasonable way, the Phase Rule may be expressed as follows, without any need of reference to the number of "components" as usually defined:

$$F = (n_i + n_E) - (n_\phi + n_r) \quad (1)$$

in which F = the actual variance, or the number of degrees of freedom in the special case; n_i the number of individuals as defined above; n_E the number of physical manifestations of energy (mechanical, thermal, electrical, etc.) which are brought into play in the reaction; n_ϕ the number of phases; and n_r the number of independent restrictions or fixed conditions which are determined by the circumstances of the case, but not included in the definition of the individuals. Each quantity is, of course, a small whole number. This method of statement separates sharply the characteristics (n_i and n_E) tending to *increase* the variance, from those (n_ϕ and n_r) tending to *diminish* the variance, and seems to me to place the whole subject in a clearer light.

Ordinarily where only mechanical and thermal energy come into play, $n_E = 2$. Then the equation for the Phase Rule becomes

$$F = (n_i + 2) - (n_\phi + n_r) \quad (2)$$

This is, of course, the ordinary statement of the Phase Rule, with the addition of n_r , the number of restrictions, as a last term. Equation 2 thus given is used in the subsequent exemplification.

Because all the subtlety of the Phase Rule is concentrated in the last new term, n_r , one must be especially careful in studying each case to be sure that the value of this term is properly estimated—in other words, to be sure that one has counted correctly all the independent restrictions. Moreover, each restriction (especially those concerning concentration, which apply to a variable phase) must be carefully examined in order to show that it is really not involved in another previously determined upon or in the definition of the individuals. This procedure, of course, involves thought, but I know of no method by which the Phase Rule can be applied properly to any but the simplest cases without thought, according to any definition. One must remember, of course, that no restriction can be applied to the quantity of any *phase*; a drop of a solution in true equilibrium is as effective as a bucketful for the purposes of the Phase Rule. Thus in the case of calcium carbonate discussed below, a limitation of the quantity of the carbon dioxide to that of the lime is not a real restriction. Adding more lime has no effect on the equilibrium.

In most cases no great difficulty arises in the interpretation of the new term n_r . So far as I can discover it may include only two different classes of restrictions; on the one hand, the intensity-factor of some form of energy may be restricted, or kept constant; on the other hand, one in-

dividual may (either from chemical necessity or arbitrary choice) be kept in definite weight-ratio to some other individual, or at definite concentration in a variable phase.¹ This duality of type might be indicated if desired by substituting for n_r its equivalent $n_{r'} + n_{r''}$, in which the two modified subscripts represent the two different types. A new restriction belonging to either of these types adds one to their sum n_r . For example, if temperature and pressure are both fixed, but no other fixed requirements exist, $n_{r'} = 2$ and $n_{r''} = 0$, therefore, $n_r = 2$. If neither temperature nor pressure is fixed, but one individual must always bear a definite quantitative relation to another, $n_{r'} = 0$ and $n_{r''} = 1$, therefore, $n_r = 1$.

It will be noted that the usual definition of the number of "components" makes this number equal to $(n_i - n_{r'})$.

Let us interpret individual cases in the light of the Phase Rule equation given in terms of chemical individuals. For example, let us take the familiar case of the decomposition by heat of calcium carbonate. There we have the individuals $\text{CaO} + \text{CO}_2$, that is $n_i = 2$. When the two solids and gas are present in equilibrium $n_\phi = 3$, of course. If no restriction is placed on the concentration of the variable gas phase (or on the pressure or temperature of the gas) $n_r = 0$. Therefore, $F = 1$, that is, the system is univariant.² If either temperature or pressure is fixed, $n_r = 1$ and $F = 0$.

Another familiar case is the case of steam, oxygen and hydrogen in equilibrium at a high temperature, the hydrogen and oxygen being in equivalent proportions resulting from the decomposition of water. The usual definition of component would give only one component to this system, but many chemists may be better satisfied by taking, according to the definition given above, hydrogen and oxygen as the "individuals" concerned making $n_i = 2$. As there is only one phase, $n_\phi = 1$; and here $n_r = 1$, because a restriction is placed on the ratio of concentrations of the oxygen and hydrogen in the single phase, which is a variable one. Therefore, $F = 2$, and the system is bivariant.

It may be noted that the essential question of this kind of restriction is concerned with the variable phase, and involves the relative concentration of the individuals in this phase. The variable phase always holds the key to the situation.

Taking a more complicated case, we see that the definition applies equally

¹ The requirement that a given volume of gas shall contain a given weight is a valid restriction in this sense.

² Let me urge once more the use of the purely Latin terms univariant, bivariant, etc., as indicating the degrees of freedom instead of the hybrid Greek-Latin terms monovariant, etc. This consistent terminology was suggested in 1898, *Am. J. Sci.*, [4] 6, 201 (1898)). It has been supported also by Trevor, but has not always been adopted.

well, for example, to a mixture of a dilute solution of sodium bromide and potassium chloride in equilibrium with its vapor. If the solution remains dilute and no new phase appears, this may be looked upon from two equally legitimate points of view. In the first place, we may take as the individuals of the system: sodium bromide, potassium chloride and water, that is, $n_i = 3$, $n_p = 2$, $n_r = 0$, therefore $F = 3$. On the other hand, we may look upon the individuals as the four ions Na' , Br' , K' , Cl' (or the four corresponding elements) and water—five in number—bearing in mind later the two independent restrictions: concentration $\text{Na} = \text{concentration Br}$; and concentration $\text{K} = \text{concentration Cl}$. According to this better interpretation, we should have $n_i = 5$, $n_p = 2$, $n_r = 2$, therefore, $F = 3$ as before.

As regards the former of these interpretations, trouble begins, in a case of this kind, when the solution is so far evaporated that a meta-theoretical product separates out; or when a new salt containing the same elements (*e. g.*, sodium chloride) is added. In that case, although the elements and ions present remain the same, a new individual, in the sense used in this interpretation, has really been added, and the old, usually accepted explanation is somewhat puzzling, although it is legitimate.¹

On the other hand, the latter interpretation involving five individuals, which is now demanded by the strict phraseology of the definition of the term, offers no difficulty whatever. Thus if with this system sodium chloride separates (both the other salts being decomposed in the process, but the five individuals remaining unchanged), the two restrictions named above have merged into one.² $\text{Conc. (K + Na) = conc. (Cl + Br)}$; and the new freedom is exactly offset by the new phase: *i. e.*, $n_i = 5$, $n_p = 3$, $n_r = 1$, therefore, $F = 3$. Similar reasoning is involved if a little sodium chloride is dissolved in the dilute solution of KCl and NaBr without causing the appearance of a new phase; but here, of course, the result is $F = 4$.

These considerations and others lead me to the conclusion that the use of the conception of chemical "individuals" as defined above gives greater flexibility and clearness than the usual way of first calculating components and then considering those in the Phase Rule equation.

The mathematical verification of Equations 1 and 2 follows directly, it seems to me, from that of the old familiar Phase Rule equation; they are really only different methods of stating the same idea.

Perhaps it may be worth while to give here a brief statement of an inductive method of presenting the Phase Rule, which I have found very efficacious for beginners. Doubtless others have used this method, but

¹ See for example Bancroft, "The Phase Rule," p. 230 (1897).

² It is true that this restriction existed in the system before the NaCl was added; but it was not independent of the other two previously present.

I do not know of its having been published, and it was independently evolved here.¹ After the student has become familiar in the laboratory with such well-known phenomena as the dependence of boiling point and freezing point on pressure and their definiteness under constant pressure, with one individual; and after he has further made himself practically acquainted with the boiling points and freezing points of definite solutions, and with cryohydric and transition points and kindred phenomena, his knowledge may be summed up in the following table:

With one individual, a fixed point (where $F = 0$) is determined by:

	Total fixed conditions.
The coexistence of 3 phases.....	3
The coexistence of 2 phases and definite pressure.....	3
The coexistence of 2 phases and definite temperature.....	3
The coexistence of 1 phase and definite pressure and temperature.....	3

With two individuals (e. g., H_2O and Na_2SO_4), a fixed point is determined by:

The coexistence of 4 phases.....	4
The coexistence of 3 phases and definite pressure.....	4
The coexistence of 3 phases and definite temperature.....	4
The coexistence of 2 phases and definite pressure and temperature.....	4
The coexistence of 2 phases and definite temperature and defined concentration.....	4

The same method may be extended to more complicated systems and enforced with diagrams, which make clear the fixity of these several points. The student thus sees that three fixed conditions are necessary for invariance with one individual, four fixed conditions with two individuals, five fixed conditions with three individuals, and so on. He sees further that the restricting of any of the variable conditions produces exactly the same effect as the addition of another phase. Thus he perceives that it is legitimate to add n_r to n_p in the expression for the Phase Rule. Of course, the number of degrees of freedom are simply the number of additional restrictions which it is necessary to add to any given system in order to attain invariance.

After the student has become thoroughly familiar with examples in which pressure and temperature are the only energetic intensity-factors to be considered, other manifestations of physical energy may be brought in, and the student is shown the effect of changing surface tension produced by variation in the size particles with its consequent effect upon solubility, the question of electromotive force, etc., using Equation 1 above.²

¹ Essentially the same method has been suggested, but not amplified, in the clear explanation of the Phase Rule in "General Principles of Chemistry," by A. A. Noyes and Sherill, p. 95 (1914).

² As Trevor has pointed out (*J. Phys. Chem.*, 1, 349 (1897)), the ordinary two-fluid "reversible" cell is not in true equilibrium because of the osmotic pressure and diffusion at the junction of the two liquids. The beginner is, therefore, advised not to

This outline is, of course, merely a sketch of the method. It needs amplification with the help of many examples, which can easily be provided by anyone even moderately familiar with the principles evolved.

Summary.

To sum up briefly the contents of this note: the idea of the component is replaced by that of the "individual," which is defined in the simplest possible way as an undecomposed chemical substance necessary for constructing the system under consideration, and the number of individuals needed to satisfy the Phase Rule is taken as the least number of such "individuals" needed to construct the system. Into the equation representing the Phase Rule and expressing the number of degrees of freedom of the system is then introduced a term giving the maximum number of independent restrictions involved in the fixation either (a) of one or more of the intensity-factors of the forms of physical energy concerned, or (b) of some concentration-relation of the individuals in the variable phase. A somewhat obvious method of evolving the Phase Rule inductively for beginners is sketched.

This note is intended rather as the suggestion of an idea than as a final or complete statement of the case. The nomenclature is subject to change if better designations can be found. The object of the note is to remove, if possible, the most serious stumbling-block from the path of the beginner.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

THE COMPRESSIBILITY OF CERTAIN TYPICAL HYDROCARBONS, ALCOHOLS AND KETONES.

BY T. W. RICHARDS AND J. W. SHIPLEY.

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This research was a continuation of work already published in several instalments during the last twelve years. The object was to ascertain a large number of compressibilities of pure organic substances under similar conditions. From a physicochemical point of view this is a desirable object, because compressibility has close relations to other properties and is directly concerned with the nature of the several substances.¹

attempt the application of the Phase Rule to such cases, which are full of pitfalls. A much simpler case is a dilute amalgam cell with two concentrations of amalgam as the two electrodes. Here the concentration of the electrolyte is without influence and does not form another restriction (Richards and Lewis, *Z. physik. Chem.*, 28, 7 (1899)).

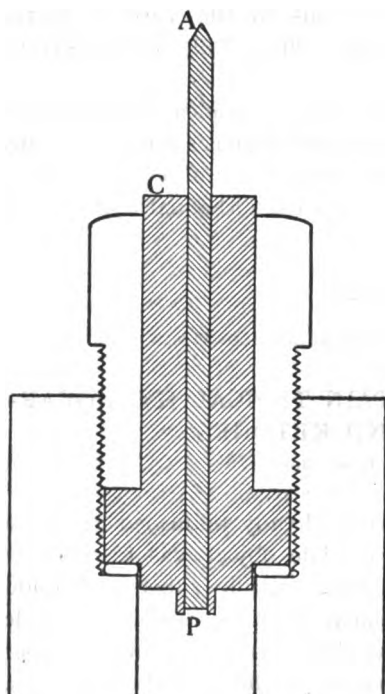
¹ Richards and Stull, *Pub. Carnegie Inst.*, 7 (1903); *Z. physik. Chem.*, 49, 1 (1904); Richards, *THIS JOURNAL*, 26, 399 (1904); Richards, Stull, Brink and Bonnet, *Pub. Carnegie Inst.*, 76 (1907); *Z. physik. Chem.*, 61, 77 (1907); *Ibid.*, 61, 183 (1907); *THIS*

The previous papers have so fully described the method that only a very abbreviated description will be given here, emphasis being laid merely upon the respects in which improvements have been introduced. The most important improvements were in the pressure gauge, the form of piezometer and the study of the hysteresis of glass.

It should be noted that the present research was completed before that carried out with the help of E. P. Bartlett¹ upon the compressibilities of several elements, and the experience gained in the present research was very useful in that one.

Pressure Gauge.

The absolute pressure gauge resembled in principle those of Amagat and Bridgman, but was smaller and comparatively inexpensive, although fully as accurate. It consisted simply of a steel attachment to be screwed upon the pressure-cylinder of the familiar Cailletet apparatus—the



attachment being bored with a very even hole, into which ran a closely fitting cylindrical piston or plunger. The shaping of this attachment and the manner of screwing it in place upon the pressure cylinder are shown in the diagram (Fig. 1) which will be at once comprehensible to anyone familiar with the Cailletet apparatus. The projecting conical upper end of the plunger was fitted loosely into a conical bearing, and this supported a horizontal steel bar, from which was suspended a heavy scale pan made of oak, about 50×100 cm. in area, and capable of bearing weights to the extent of 200 kg. The plunger and cylindrical hole were about 0.63 cm. ($1/4$ inch) in diameter.

Two such attachments (A and B) were made for us with great care by the Taft-Pierce Mfg. Co. of Woonsocket, R. I., and their indications were found both at once to the same system.

Fig. 1.—Plunger and cylinder of absolute pressure gauge. Plunger AP, to be precisely identical when attached cylinder C.

JOURNAL, 31, 154 (1909); Richards and Mathews, *Ibid.*, 30, 8 (1908); *Z. physik. Chem.*, 61, 449 (1908); Richards and Jones, *THIS JOURNAL*, 31, 158 (1909); *Z. physik. Chem.*, 71, 152 (1910); Richards, Stull, Mathews and Speyers, *THIS JOURNAL*, 34, 971 (1912).

¹ Richards and Bartlett, *THIS JOURNAL*, 37, 470 (1915).

Especial study was made of the heretofore doubtful question as to the actual working diameter of the plunger, compared with its carefully measured diameter when not in operation. The latter can be determined with great accuracy by means of a screw micrometer gauge, which gives very precise results; but the diameter while in operation is not so easily estimated, partly because the space between the plunger and the cylinder must be appreciable if the cylinder is to move easily, and partly because of the compression of the steel piston. The latter effect is negligible at 500 atmospheres, however, not exceeding 0.06%.

In practice, previous experimenters have usually accounted half of the width of the intervening space between plunger and cylinder as belonging to the plunger and half of it as belonging to the cylinder, thus accounting the effective diameter of the plunger as the mean between that of the cylinder and the plunger; but no one seems to have made a careful quantitative study as to the legitimacy of this procedure. We at first adopted the same method and determined the size of the annular space by exactly filling it with oil and then withdrawing and weighing the plunger. Several trials gave very consistent results, and the method (which depended upon the assumption that upon withdrawal half of the oil remained on the plunger and half on the cylinder) would doubtless have answered any ordinary purpose. Nevertheless, we were not satisfied, and proceeded to test the behavior of plungers B_1 , B_2 , B_3 , of slightly different sizes in the same cylinder, comparing each with A_1 in a connected apparatus. The size of the bore at P was measured by means of a very slightly tapering plug made for this special purpose, and the plungers were measured with great care micrometrically. The following table contains the result of these measurements, together with the comparison of the calculated effective area with that actually found by the comparison of the pressures. It will be seen that the agreement is satisfactory—the greatest error being only 0.02%, except with the loosest piston, which gave a result well within 0.1%.

TABLE I.—EFFECTIVE PLUNGER AREA (IN INCHES).

Plunger.	Diameter of plunger.	Diameter of lower orifice of cylinder.	Double width of vacant annular space.	Assumed effective diameter.	Effective area calculated from assumed effective diameter.	Difference between calculated effective area and that of A_1 .	Difference found in actual effec. area by direct compar. with A_1 .
A_1	0.25040	0.25049	0.00009	0.25045	0.31784	0.00000	0.0000
B_1	0.24997	0.25000	0.00003	0.24999	0.31670	0.00114	0.0012
B_2	0.24970	0.25000	0.00030	0.24985	0.31630	0.00154	0.0016
B_3	0.24950	0.25000	0.00050	0.24975	0.31605	0.0018	0.0020

In a second trial these gauges were compared not only with one another, but also, taking great care and expenditure of time, with Dr. Bridgman's gauge. In this comparison the least accurate plunger (B_3) was not

included, but the comparison of the other plungers was even more satisfactory than the figures in the table just given. B_1 was not taken as the standard, because it fitted very closely indeed. Assuming its area as 0.31670, Bridgman's piston was found to have the actual area calculated from the weights which it would support, of 0.31842, whereas we calculated its area by adding half the width of its annular space to its radius as 0.31845. In the same way for A_1 0.31785 was found as against the calculated 0.31784, and for B_2 the value 0.31627 instead of the calculated 0.31630. In no case does the deviation here amount to as much as 0.01%; the agreement is so close that it must have been partly due to accident. In any case the usual rule of accounting half of the width of the annular space as belonging to the piston is seen to be a safe and adequate rule. Moreover, it is clear that we had attained very exactly a knowledge of the diameters of our several pistons, and that, therefore, our standard of pressure was beyond reproach.

The details of the comparison of Bridgman's gauge with ours need not be dwelt upon. It is enough to say that all the pressures given in the present paper are determined by one or other of the pistons just described, and that all of these gave the same standard of pressure within the limit of error of the experiment, agreeing also with Bridgman's. The Bourdon gauge was used only as an approximate guide to the pressure and never as a final index.

Piezometer.

The piezometer for liquids was designed with the idea of securing the greatest possible convenience and accuracy. The principle is the same as that of the forms suggested in previous papers, but it is on the whole decidedly more convenient than most of those forms. It is shown in the diagram (Fig. 2). The platinum point (opposite P) must, as usual, be very finely sharpened. The most difficult part of the apparatus to adjust was the stopcock (S), which needed polishing, first with very fine emery and finally with rouge until it was perfectly smooth. It was lubricated with a trace of lubricant made of hard and soft paraffin and melted rubber, but this was scarcely necessary, and only a trace was used. The accuracy of the apparatus depends greatly upon having the stopcock ground with extraordinary fineness. The whole must be very carefully constructed of glass as nearly similar as possible, and must be annealed with the greatest care, because any strain in the glass may lead to rupture under pressure. When constructed in this way the apparatus proved to be exceedingly satisfactory. It was at first filled with mercury between S and P, and the compressibility of the mercury in glass was determined. Then the liquid to be studied was drawn in after the mercury, the latter being drawn up into the upper barrel (A). After the excess of mercury in A had been removed, the compression of the remain-

ing mercury and the weighed amount of liquid was determined quantitatively in the usual manner by adding successive drops of mercury through the opening O and finding in each case the pressure needed to cause exact contact at the point P. The calculation was precisely as usual. Besides eliminating the objectionable stopper, which is the chief disadvantage in most of the other forms thus far suggested, this form of piezometer offered the further advantage in that the weight of the substance being compressed was determined immediately after being drawn into the apparatus.

The details of filling were as follows: After it had been thoroughly cleaned, dried, filled with mercury considerably above the platinum point and weighed, the point of the stopcock was inserted into an auxiliary vessel containing an accurately weighed quantity of mercury, together with about the desired quantity of the liquid (9 or 10 cc.) to be compressed. Enough mercury was expelled from the piezometer into the auxiliary vessel below to drive over all the air enclosed in the stopcock. Then most of the liquid to be studied (7 to 8 cc.) was drawn up into the apparatus, followed by mercury sufficient to form a seal 10 cm. long in the capillary above the stopcock. The mercury in the stopcock itself was then run back into the auxiliary vessel by turning the stopcock one-quarter way around until the interior hole was opposite to the aperture (H) drilled for this purpose, and the piezometer with its contents was reweighed. The residual lighter liquid remaining in the auxiliary vessel was removed, and the weight of the mercury in the auxiliary vessel was determined after thorough drying with filter paper. The gain of the weight of the piezometer vessel and total mercury before and after gave the weight of substance introduced into the piezometer. In practice this method was found to be very expeditious and exact and the manipulation easy and neat.

After the last weighing, the mercury in the upper barrel A was removed by a fine pipet down to the platinum point P. It is absolutely essential that the small mercury meniscus thus left should be perfectly clean. Otherwise good contact is not always obtained at the platinum point, and the indications of the in-



Fig. 2.—Piezometer for liquids. The platinum point which determines the attainment of definite volume is opposite P.

strument are uncertain. On the other hand, when it is perfectly clean, the pressure may be ascertained within 0.01 megabar. A brief description of the method of cleaning may be given in order to guide others in this important procedure. The barrel A was filled with water, and a drop or two of concentrated nitric acid introduced by means of a capillary pipet directly upon the surface of the mercury in the capillary. By alternately slightly warming and cooling the piezometer, the acid was drawn up and down the capillary past the platinum point. This was continued with fresh quantities of acid until the mercury moved up and down without any break in its surface or tendency to cling to the walls. The acid was then washed out by means of a very fine funnel tube, and the walls of the capillary and the platinum point scrubbed with a bit of chamois on the end of a wire.

Subsequently, of course, great pains must be taken to exclude the access of foreign matter to this carefully cleaned spot. The upper bulb A was plugged with cotton wool at its top (O), but even this does not wholly prevent the creeping of oil along the glass or wire when the instrument has been some time in use after filling. After each determination of the pressure the plug was removed, and the adhering oil dissolved with a little ether, care being taken that none of the latter approached the surface of the mercury. Since it is difficult to obtain ether pure enough to be wholly without action upon mercury, the water in bulb A must be completely renewed after each determination of pressure.

If these precautions are heeded, very constant results may be obtained. The mercury meniscus evidently takes exactly the same shape at each return to any definite pressure. The meniscus may still change slightly in shape at different pressures, but this makes no difference whatever in the result obtained by this method, for any changes of this sort are entirely eliminated in subtracting the values obtained with mercury alone from those obtained with the given liquid in the piezometer.

The bulb B was immersed wholly under mercury in the barrel of the compression apparatus, and was found to lose very quickly its heat of compression. If the pressure is slowly applied, the temperature of the whole apparatus never rises much above the constant temperature of the thermostat—an important condition on account of the thermal hysteresis of glass. The reading was always taken 15 minutes from the first application of pressure. The piezometer being always lighter specifically than mercury, it was necessary to push the instrument down beneath this liquid, and the pressure thus applied in mounting the instrument kept a platinum coil emerging from the top of A in good contact with a similar small coil attached to the movable top of the cylinder, so that electrical connection was easily obtained. This arrangement is the simplest

and most convenient method of arranging the instrument and making contact thus far devised.

The capillary pipet employed for removing and adding mercury is worth a brief mention. The fine tube 25 cm. long was graduated in terms of grams of mercury, and was of such diameter that 2.5 cm. corresponded to one gram. This greatly facilitated removing or adding a definite amount of mercury to the piezometer. Before removing the pipet from the piezometer the mercury in the capillary pipet was always drawn up several centimeters from its lower end, in order to avoid the possibility of losing drops of mercury when transferring it to the weighing cup.

Two piezometers of this shape were used, designated IV and V. The latter contained the same stopcock as the former, which was accidentally broken in the middle of the research.

In connection with this work, a careful series of experiments on the pressure-volume hysteresis of glass was conducted. It was found that this may be very important, if the glass is exposed to high pressure for a long time. Glass slowly contracts under the continued pressure, so that the piezometer diminishes in volume. At first it would seem as if this pressure hysteresis would have a detrimental effect, but this is not the case. If the same time is always allowed between the first application of pressure and the final reading, and if on successive days the instrument is treated in essentially the same way with each successive liquid, as well as with the mercury used in standardizing it in the first place, all these hysteresis effects are eliminated, being the same in each case. Hence in working with the glass apparatus at pressures above 200 megabars, one must be careful to comply with these conditions if results of the highest accuracy are desired. Fortunately, this precaution has been observed in all the work of this sort at Harvard since the beginning in 1902. Of course, the slight volume changes caused by this continued action of pressure have very much less percentage effect upon organic liquids than upon mercury. Nevertheless, it is worth while so to arrange one's experiments as to avoid any error even in the present case.

The full details of the work on pressure-volume hysteresis of glass will be given in another place. They do not concern the present investigation, since the effect was here eliminated in the way just described.

Preparation and Purification of Materials.

Among aliphatic compounds, two nonanes, 2,5-dimethyl heptane and 2,4-dimethyl heptane, were studied, as well as methyl and ethyl alcohol, acetone and diethyl ketone. Eight homologous aromatic substances—benzene, toluene, ethyl benzene, isopropyl benzene (cumene), normal propyl benzene, tertiary butyl benzene, mesitylene and pseudocumene—were subjected to qualitative compression, as well as cyclohexane (hexamethylene) and two of its derivatives, cyclohexanol and cyclohexanone.

These substances were chosen partly to fill gaps in previous work, and partly because they represent a wide variety of carbon compounds.

The preparation and purification of the substances compressed took much time. Although they were secured in the purest condition obtainable yet in most cases they were many times further fractionated. In most cases the constancy of the boiling point and the density were taken as criteria; but in two cases the constancy of the freezing point as solidification progressed could be used as a yet safer assurance of the purity of the substance; in such cases the purification was best conducted by freezing. The full description of the preparation and purification of the substances would require too much space for this publication. Their degree of purity may be inferred from their physical constants given in the table immediately following.

The aromatic hydrocarbons were all the same preparations as those used in a recent paper by one of us and Dr. Frederick Barry.¹ *Methyl alcohol* was prepared in a very pure state through methyl oxalate, which was recrystallized from water until free from impurity and carefully saponified, when the alcohol was fractionally distilled, treated with iodine and sodium hydroxide, and again fractionally distilled. *Acetone* was purified through the acid sulfite addition-product, as was also *cyclohexanone*.

TABLE I.—PHYSICAL CONSTANTS OF SUBSTANCES EMPLOYED.

Name.	Boiling point.	Barometer.	Melting point.	Density 20°/4°.
Methyl alcohol.....	64.48° to 64.55°	760	...	0.7923
Ethyl alcohol.....	78.4°	753.5	...	0.7903
Acetone.....	55.8° to 55.9°	752.3	...	0.7915
Diethyl ketone.....	101.2° to 101.3°	760	...	0.8136
2,5-Dimethyl heptane.....	135.6° to 135.9°	760	...	0.7198
2,4-Dimethyl heptane (A).....	132.9° to 133°	760	...	0.7158
2,4-Dimethyl heptane (B).....	132.4° to 132.9°	760	...	0.7162
Benzene.....	79.70° to 79.71°	763	5.483°	0.8791
Toluene.....	110.3° to 110.4°	756	...	0.8649
Ethyl benzene (A).....	136.3° to 136.4°	766.7	...	0.8678
Ethyl benzene (B).....	136.4° to 136.5°	766.7	...	0.8697
Isopropyl benzene (cumene).....	152.6° to 152.8°	759	...	0.8620
Normal propyl benzene (A).....	157.9° to 158.2°	765	...	0.8616
Normal propyl benzene (B).....	157.9° to 158.2°	765	...	0.8617
Tertiary butyl benzene.....	168.6° to 168.7°	759.0	...	0.8671
Mesitylene.....	164.8° to 164.9°	760	...	0.8634
Pseudo cumene.....	169.4° to 169.6°	764.8	...	0.8786
Cyclohexane (liquid).....	81.3° to 81.5°	760	6.40°	0.7791
Cyclohexane (solid).....	6.40°	0.8230
Cyclohexanol (solid) ²	23.87°	0.9624
Cyclohexanone.....	155.6° to 155.7°	768.0	...	0.9466

¹ Richards and Barry, *THIS JOURNAL*, 37, 993 (1915).

² Furthermore, the density of liquid cyclohexanol at 40.0°/4° was found to be 0.9327, and at 34.16°/4°, 0.9369; and its boiling point 160.8°.

This latter substance, as well as *cyclohexanol* and *cyclohexane* were made for us by Dr. G. L. Kelley by the Sabatier-Senderens method. The former of the last two (which is very difficult to dry) was purified by 24 recrystallizations, and the latter by 4 recrystallizations. The *nonanes*, two in number, were kindly made by Dr. Latham Clarke¹ for this investigation. All these substances except cyclohexanol and cyclohexanone were scrupulously dried, usually by means of finely powdered fresh lime or sodium. *Mercury* and *water* were carefully purified by the recognized methods used in every laboratory.

In Table I the physical constants of the several substances are recorded. In three cases two samples were available. In only one of these cases, namely, that of ethyl benzene, were the properties of the two samples different to an important degree. Here, Sample A (made by the Fittig reaction) was purer than Sample B (made by the Friedel-Crafts reaction) for reasons explained in the paper with Barry. In the case of propyl benzene a similar difference of source made no difference in the resulting substance.

Data and Results.

Eight determinations of the compressibility of water were made from time to time in order to test the constancy of the method as well as the effect of dissolved air in water. These need not be given in detail here; they will be recorded in another place. It is enough to say that the average compressibility of water over 500 atmospheres remained constant within the limit of error of experiment throughout the whole time. This average was 43.26 between 100 and 300 megabars, 40.69 over the next 200 megabars or an average of 41.97 over the whole range. These determinations showed: first, that the effect of dissolved air in water is less than the error of the method; secondly, that the two pressure-gauge pistons gave essentially the same results; and thirdly (since the determinations were not made all at once, but rather at intervals between those of the organic substances), that the apparatus was functioning properly throughout the time of the research.

The results obtained with the several carbon compounds are shown in Table II. They are tabulated over the same ranges of pressure, with the exception of cyclohexane, in which case (because the substance solidified during compression) the result for the liquid is given only between 100 and 200 megabars and that for the solid only between 400 and 500 megabars. In almost every case at least two complete experiments were made with each substance; and in every case the work with each substance was continued until there could be no reasonable doubt of the result. The total number of experiments made with the fifteen carbon compounds was thirty-seven.

¹ Latham Clarke, *THIS JOURNAL*, 34, 60 (1912).

The complete data occupy so much space that there is not room for them here; but they will be published in full in a monograph soon to be published by the Carnegie Institution of Washington, with complete details describing the purification of the substances.

TABLE II.—SUMMARY: COMPRESSIBILITY OF CARBON COMPOUNDS.

Temperature 20.00° (except with cyclohexanol).

Unit of pressure = megabar = megadyne per sq. cm. = 0.987 atmosphere, approximately.

	P. range 100-500.	P. range 100-300.	P. range 300-500.	Diff. between ranges.
Methyl alcohol.....	87.67	95.81	79.53	16.28
Ethyl alcohol.....	81.60	88.69	74.51	14.18
Acetone.....	90.09	98.72	81.46	17.26
Diethyl ketone.....	76.98	83.60	70.36	13.24
2,5-Dimethyl heptane.....	85.82	94.93	76.71	18.22
2,4-Dimethyl heptane.....	87.12	95.58	78.65	16.73
Benzene.....	72.09	77.66	66.52	11.14
Toluene.....	69.00	74.07	63.93	10.14
Ethyl benzene.....	65.94	70.84	60.97	9.87
Isopropyl benzene.....	65.37	70.34	60.40	9.94
Normal propyl benzene.....	64.91	69.73	60.09	9.64
Tertiary butyl benzene.....	63.44	68.23	58.65	9.58
Mesitylene.....	62.86	67.41	58.31	9.10
Pseudo cumene.....	60.18	64.26	56.10	8.16
Cyclohexane (liquid).....	...	[92.56]
Cyclohexane (solid).....	[49.04]	...
Cyclohexanol (liquid) (40.0°).....	...	55.58
Cyclohexanol (liquid) (34.16°).....	...	53.96
Cyclohexanol (solid).....	34.81	...
Cyclohexanone.....	54.41	57.76	51.06	6.70

A complete discussion of these results in relation to one another and to other similar data as well as to the other related properties of material is a subject too large for the present paper, but a few points are worthy of emphasis. The first relation which is obviously to be drawn from the data is the remarkable parallelism between change of compressibility with pressure and the magnitude of the compressibility itself. In almost every case greater compressibility goes with greater change of compressibility under increasing pressure. This is shown by the accompanying diagram, in which the compressibility over the whole range is plotted in the direction of abscissae and the difference between the result for the upper and lower halves in the direction of ordinates. Only one point is markedly distant from the fairly regular curve, namely, that corresponding to 2,5-dimethyl heptane. Whether this single discrepancy has real meaning or is due to impurity in the substance, it is impossible as yet to say. A single deviation of this kind, however, does not greatly injure the verdict of the others, since the relationship can make no claim to precise accuracy,

but only stands as an indication of a general tendency. The results clearly justify the similar but less consistent curve shown in an earlier

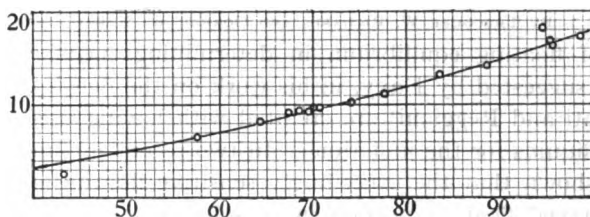


Fig. 3.—Change of compressibility with pressure compared with magnitude of compressibility. Changes of compressibility with pressure are plotted as ordinates; compressibilities are plotted as abscissae. The 16 different substances include paraffin and aromatic hydrocarbons, alcohols, ketones and cyclohexane derivatives, as well as water.

article.¹ That this new curve, which depicts more accurately determined values of a wide variety of substances, should be yet better than the earlier one is interesting and significant.

Attention should also be called to the fact that in general the more compressible substance of a given type has the lower boiling point. Compare, for example, methyl and ethyl alcohol, acetone and diethyl ketone, the two nonanes, the benzene series, and so on. Here, of course, the specific nature of the substance makes the parallelism between different classes less striking, and in the comparison of densities also the different effects of different elements prevent indiscriminate comparison. When a large number of accurate data have been obtained, these matters, none of which have as yet been fully treated, will be made the subject of an especial communication, in which the various contributory effects will be discussed in detail. We are glad to express indebtedness to the Carnegie Institution of Washington for the generous pecuniary assistance which made this work possible.

Summary.

The present paper recounts the following experimental details: First, an accurate but simple pressure gauge is described; secondly, the usual practise with regard to allowing for the space between piston and cylinder in such a gauge is justified by experiment; thirdly, data for the compressibility of 15 organic liquids are recorded, some of them for the first time; fourthly, the striking relation between the magnitude of the compressibility and the change of this compressibility with pressure is pointed out; and, fifthly, attention is called, briefly, to relationships to other properties.

CAMBRIDGE, MASS.

¹ Richards, Stull, Matthews and Speyers, *THIS JOURNAL*, 34, 990 (1912).

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

FURTHER STUDY OF FLOATING EQUILIBRIUM.

BY THEODORE W. RICHARDS AND GORHAM W. HARRIS.

The use of floating equilibrium in determining specific gravity was perhaps first suggested by Davy, in his work on the density of the alkali metals. Pisati and Reggiani¹ are credited with having used the method for studying liquids for the first time. In two recent preliminary papers² it has been shown that the exceedingly sensitive floating equilibrium of a suitably shaped float suspended in a solution of the same density may perhaps be capable of a variety of useful applications—on the one hand, to methods of chemical analysis, and on the other, to the calibration of thermometers, as well as to the study of the coefficient of expansion of the float or the liquid. The method has the virtue of being comparatively simple and inexpensive, thus being within the reach of almost anyone.

This being the case, a careful study of the especial precautions necessary for the exact prosecution of such work becomes important, and the present paper describes very briefly further experiments concerning: firstly, the precautions necessary for quick and accurate determination of the floating equilibrium; secondly, the thermal hysteresis of glass floats; thirdly, the effect of changing atmospheric pressure upon their behavior; fourthly, the effect of traces of common impurities in water; and finally, the temperatures of floating equilibria of the floats in various dilute solutions of hydrochloric acid, which afford a means of analyzing the solution or of standardizing approximately a given interval in a thermometer. Hydrochloric acid was selected as a standard substance because of its ready purification and the ease with which its solutions may be analyzed by volumetric methods. The outcome shows, as usual, that the attainment of accuracy demands thought and care; but also that useful and interesting results may be obtained with due precautions.

Apparatus and Precautions.

A thermostat capable of maintaining a constant temperature within one-thousandth of a degree and of easily altering this constant temperature at the operator's will is essential for great precision. Some such a contrivance may with advantage be at the disposal of anyone who wishes to standardize a thermometer by any method.³

¹ Pisati e Reggiani, *Rend. R. Acad. d. Lincei*, [4] 7, 99 (1890).

² Richards and Shipley, *THIS JOURNAL*, 34, 599 (1912); 36, 1 (1914). Attention is called also to the interesting, accurate and valuable work of Lamb and Lee, who balanced increased bouyancy by magnetic attraction. *THIS JOURNAL*, 35, 1666 (1913).

³ See, for example, the chapter by one of us in Stähler's "Handbuch," Vol. III, p. 259 (1912). By arranging the platinum contact point so as to be movable over a fixed scale, the shifting of the temperature is easily effected.

The method was essentially that described on page 2 of our paper of 1914.¹ The hydrochloric acid solution, in which was suspended the fish-shaped float, was protected from evaporation by a current of properly moistened air, and provided with an efficient stirrer to promote rapid adjustment of temperature. This stirrer must have a smooth bearing; if it consists of a glass rod running through a glass tube, enough glass powder may be ground off to influence appreciably the density and, therefore, the floating equilibrium temperature of the solution, even in a single day. To overcome this difficulty bearings were made of platinum foil at each end of the tube admitting the stirrer. A collar of platinum foil was slit above at intervals, and the strips bent outwards and over, and fastened here and there by means of fusible glass. With this arrangement, although traces of platinum dust were worn from the bearings, no glass was worn away, and the solution in the flask remained intact.

The floats, of the fish shape previously described, were observed by means of a small, inclined mirror outside of the flask but immersed in the water of the thermostat, and marks on the side of the flask helped to show whether the float was rising or sinking. Great pains must be taken to prevent small air bubbles from attaching themselves to the float.

Four kinds of glass were used in the floats: soft German tube, Jena tube with the red line called "Durorobax," Jena reagent glass, and the American "Nonsol." Mercury is the most convenient material for ballast.

Such floats remain constant in weight over a long period,² but their changes of *volume* soon after preparation are, however (as was suggested in one of the previous articles),³ highly important. At that time no quantitative determination was made. Accordingly, two floats were now tested in pure water over a long period from the day of their preparation, the results being given in Table I and plotted in Fig. 1.

TABLE I.—CHANGE OF FLOATING EQUILIBRIUM TEMPERATURE DUE TO CONTRACTION OF GLASS ON AGING.

Series 1.		Series 2.	
Age of float. Hours.	Float. equil. temperature.	Age of float. Hours.	Float. equil. temperature.
7	20.410°	2	19.884°
168	20.304	6	19.852
199	20.293	24	19.807
243	20.280	55	19.786
384	20.262	75	19.770
1632	20.1825	174	19.732
1687	20.1825	292	19.690
1752	20.1815	816	19.602
Total change,		0.2820°	
0.2285°			

¹ *Loc. cit.*

² Richards and Shipley, *THIS JOURNAL*, 36, 5 (1914).

³ *Ibid.*, 34, 600 (1912).

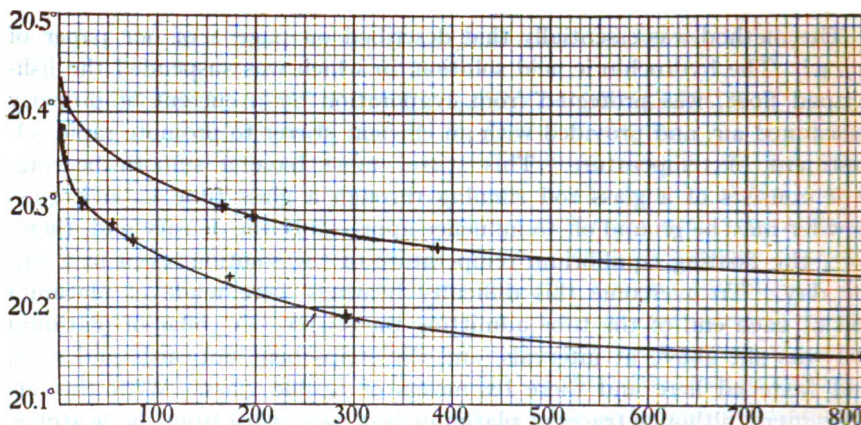


FIG. 1.—CHANGE IN FLOATING EQUILIBRIUM TEMPERATURE WITH AGE OF FLOAT.
Temperatures are plotted as ordinates, times in hours as abscissae.

The contraction in volume suffered by the floats, in the first few hours of their existence, was very serious, and even after two weeks they were still considerably decreasing in volume, from week to week. This emphasizes the caution advised in a previous paper that the floats should be old. After two months, however, the change is very slow. The latter part of each of these curves is almost exactly logarithmic, and can be, therefore, extrapolated. When this is done, it becomes clear that after three or four months the floats must be altering so slowly in volume as not to affect appreciably any ordinary use to which they might be put within a moderate interval of time. More change of volume happens within the first week of the life of a float than in all the rest of its existence put together. The total changes (corresponding to 0.2° or 0.3° in the floating equilibrium temperature) are of the order of 0.005% of the volume. This is, of course, about the order of the changes measured by the rise of the zero point of a mercury thermometer after aging. Doubtless, also, similar but far less marked changes in the volumes of the floats occur because of less violent heating or cooling; hence, for the most accurate work it is important that the floats should have been previously kept at about the temperature of the room for a long time.

The floats were washed thoroughly, and thereafter handled only with glass, double-pointed, curved forceps.

During early trials, rapid agitation of the solution contained in the insulated receptacle was found to cause electrostatic effects, which gave irregularities at first incomprehensible. The trouble was naturally most prominent when the stirrer was lifted above the surface and quickly plunged beneath it, carrying air beneath the surface. Perhaps this trouble was the cause of the irregularity in a curve noticed in one of the pre-

ceding communications. When, however, the stirrer was always kept below the surface of the solution, and a grounded platinum wire dipped into the liquid, no further trouble was experienced. Negative results obtained in air from a special bulb prepared with a sealed-in platinum wire showed that the electrical charge *within* the float, due to friction of mercury, must be very small.

Preparation of Materials.

The substances used in the work to be described were prepared with care. The water used for all solutions had been three times distilled, once from alkaline permanganate, and once from dilute sulfuric acid. In almost all cases it was used within twenty-four hours of the last distillation, and was kept in borosilicate glass flasks. That it remained constant for a long time when thus preserved was shown by the fact that the floating equilibrium temperature in water which had been preserved in a stoppered borosilicate flask for two months was found to be exactly the same as that in the freshly prepared water. Thus the amount of glass dissolved in two months was too small to be detected, even by this very sensitive method.

"Chemically pure" hydrochloric acid diluted to about 20% was distilled through a quartz condenser, and the first third of the distillate discarded. The pure middle portion was at once diluted with purest water about half strength and kept in paraffin-lined bottles.

The sodium hydroxide used for titration of the acid solutions was freed from carbon dioxide by usual methods and was kept in paraffin-lined bottles protected from carbon dioxide.

The Effect of Dissolved Paraffin and Air on the Floating Equilibrium Temperature.

The solubility of paraffin in water might seriously affect a method so sensitive, hence its amount was approximately estimated. Very pure water, which had been kept in a paraffin-lined bottle for nearly three months, when evaporated in platinum left a volatile residue (doubtless paraffin) of 0.9 mg. and only a negligible weight of nonvolatile impurity. The conclusion that such a weight of this impurity (having a density near that of water) was not important was confirmed by experiments comparing the floating equilibrium temperatures of fresh water, and of similar water which had been stored for ten weeks in a paraffin-lined bottle. The temperature with the latter was found to be 0.0005° below the former, but this is about the limit of accuracy of the method. Hence the amount of paraffin dissolved by a liter of water has an effect on its density so slight as not to alter appreciably the floating equilibrium temperature, which would be perceptibly affected (to the extent of 0.001°) by a change of density of about 0.000001.

The effect of dissolved air on the density of water and of the dilute solutions employed might also affect the floating equilibrium temperature. No difference, however, could be detected in the following trials, which were all carried out in a single day under constant pressure. The results follow:

Temperature with air-saturated water.....	20.1825°
Temperature with water freed from air by boiling and freezing.	20.1825°
Temperature with the same water shaken with air.....	20.1825°

This is not very different from the result of Marek, who found at 21° (extrapolated) no appreciable effect in the seventh decimal place by saturating water with air. At 20°, on the other hand, he found a decrease of density thus caused of 0.0000004, which would correspond to about 0.003° in the floating equilibrium temperature. This latter amount could be easily and certainly detected. Hence we are inclined to think, because we observed no change whatever, that Marek's change of 0.0000004 in the density of water at 20°, due to the saturation of air, is too large, and should be nearer zero. It is perhaps worth noting that Chappuis¹ found an average value, between 5° and 8°, about 0.00000035 less than Marek's over this range. If this same correction is applied throughout Marek's work, his result would correspond very nearly to ours. Undoubtedly, if the percentage of dissolved carbon dioxide varied greatly, differences would be observed. Our experiments were made with air under usual conditions, which are fairly constant.

Analysis of Solutions.

Ordinary volumetric analysis being too crude for so exact a process, our solutions were analyzed titrimetrically by means of weight burets, consisting of 0.1 liter Jena flasks fitted up like miniature analytical "wash-bottles" with long outlets, and provided with capillary jets. Methyl red was used as the indicator, and sufficient precautions were taken to exclude carbon dioxide. It was ascertained that the accuracy attained was adequate for the problem in hand. A permanent solution was used for comparison of the end point, made of a very dilute solution of potassium dichromate and cobalt chloride in hydrochloric acid so prepared as to match exactly the tint of methyl red in a solution known to be neutral.

The Effect of External Pressure.

The effect of changing pressure upon the density of water is well known, but the similar effect upon the glass float cannot be predicted beforehand because this depends upon the quality and thickness of the glass as well as upon the shape of the float. The correction, therefore, must be empirical, like the similar correction applied to the thermometer, which also must be taken into account. This later effect, as carefully determined.

¹ "Trav. Bureau Int.," 14D (1910).

varied with different instruments between 0.0022° to 0.0029° for one cm. of mercury.

Obviously, increase in barometric pressure by compressing the liquid tends to raise the equilibrium temperature, but, on the other hand, by compressing the float tends to lower the equilibrium temperature, and the net correction is the difference between these two effects.¹

This net correction was found experimentally, partly from readings taken at different times when the barometer was fluctuating, and partly by artificially altering the pressure.

TABLE II.—EFFECT OF PRESSURE ON FLOATING EQUILIBRIUM TEMPERATURE (CORRECTED FOR EFFECT OF PRESSURE ON THERMOMETER).

		Corr. per mm.
Float I	Soft glass.....	-0.00041°
Float J	Jena reagent glass.....	$+0.00006^{\circ}$
Float M	Jena reagent glass.....	$\pm 0.00000^{\circ}$
Float K	Durorobax glass.....	$+0.00002^{\circ}$

A negative correction indicates that the float was less compressible than the water, and a positive that it was more compressible than the water. Except in the case of the large, thick-walled float of German glass, I, it is seen that the net effect is almost nothing at all, the two corrections counterbalancing one another, that is, the average compressibility of a thin-walled float of 7 cc. volume may be made very nearly equal to that of water. The larger thin float employed by Lamb and Lee was much more compressible.

Thus the effect of pressure must never be forgotten in work of this kind. Obviously a somewhat compressible float is more suitable than a highly incompressible one, as the net correction is then smaller; moreover, even the difference in pressure between the top and bottom of the flask may have a serious effect upon the equilibrium of a very thick float. Such a float as Float I had its floating equilibrium temperature altered 0.003° in 20 cm. depth of water, so that when the flask is at equilibrium temperature with the float at the middle, the solution on the top was 0.0015° above the equilibrium temperature at that point, while that at the bottom was the same amount below. The float would, therefore, remain suspended in the middle and not be very sensitive to changes of temperature. Much more sensitive results are obtained with a float thin-walled enough to approach in compressibility that of the liquid.

The Thermometers and Temperature Scale.

The thermometers used were instruments of high grade, partly Beckmann thermometers, and partly thermochemical thermometers made to cover the range between 15° and 20° , as well as two instruments of larger range; and they were verified by reference to Baudin instruments which

¹ See Lamb and Lee, *Loc. cit.*, p. 1676.

had been very carefully standardized in Paris and elaborately studied here. They were thus all referred to the international hydrogen scale as exactly as possible under the circumstances.

Relation of Floating Equilibrium Temperature to Concentration with Hydrochloric Acid Solutions.

The method was extremely simple. The temperatures of floating equilibrium of the several floats in pure water in the neighborhood of 15° or 16° were first determined. Hydrochloric acid in definite amount was then added, and the temperature of the thermostat raised in steps until the exact floating equilibrium temperature of each float was successively reached; afterwards more hydrochloric acid was added, and so on. The amounts of added hydrochloric acid were often chosen so that the temperature would rise nearly a definite fraction of a degree. In each case portions of the hydrochloric acid were removed and carefully analyzed.

The main factors determining ease in detecting the equilibrium point are high coefficient of expansion and low viscosity. Alcoholic solutions, such as were described in the paper of 1912, are therefore especially favorable. The method works much less rapidly in a very dilute aqueous solution at 16° than in either of the solutions described in the previous papers; hence the present case is an unusually exacting one. Nevertheless there was no difficulty in securing the end point of floating equilibrium within 0.0005° if sufficient patience was employed. If, as is often the case, an accuracy within 0.01° is all that is required, the operation is much quicker and more convenient. Ordinary volumetric analysis is then sufficient, and the end point can be very quickly determined, because of the quick rising and falling of the float within the wide temperature limits permitted. Many of the precautions and corrections required in the more exact work become unnecessary. For example, the difficulty from currents produced by agitation or convection is scarcely noticeable, and the effect of changed barometric pressure on the float and solution becomes negligible.

The floating equilibrium temperatures of the five floats in several concentrations of pure dilute hydrochloric acid are given in Table III.

TABLE III.—EQUILIBRIUM TEMPERATURES AND CONCENTRATIONS.

Float J (Jena).	Float M (Jena).	Float I (soft glass).	Float K ("Durobax").	Float L ("Nonsol").	Conc. of HCl (per cent by weight).
15.172	14.823	14.962	15.387	0.00000
16.178	15.776	15.953	15.996	16.412	0.02825
17.080	16.696	0.05547
18.093	17.730	18.051	17.961	18.344	0.08874
19.064	18.725	0.12282
19.925	19.599	19.827	0.15475
24.698	24.464	25.025	24.671	0.36368
....	32.362	0.79457
....	32.337	0.80833

The portion of these data between 14° and 20° is indicated by the five upper curves on the accompanying diagram (Fig. 2). The higher points were not included in order not to diminish too greatly the scale,

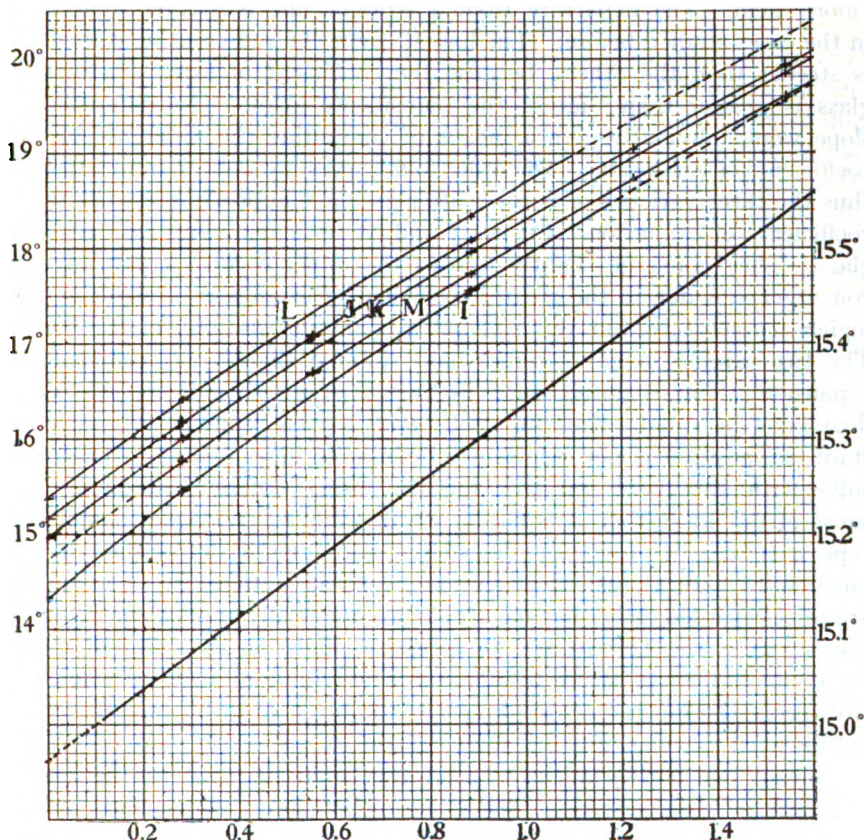


FIG. 2.—FLOATING EQUILIBRIUM TEMPERATURES IN DILUTE HYDROCHLORIC ACID.

Temperatures are plotted as ordinates, concentrations of hydrochloric as abscissae. The left-hand temperatures refer to the five uppermost curves, the right-hand only to the lowest curve. The abscissae numbers refer to grams per liter on the five upper curves, and decigrams per liter on the lowest. J and M are with reagent Jena glass floats; I, common soft glass; K, "Durorobax;" L, "Nonsol." In plotting 0.500° has been subtracted from each temperature in the case of Float I, so that its curve would not conflict with the others. The lowest curve is a ten-fold enlargement of the first part of K. The five upper curves, of course, are not on a scale large enough to show the full possibilities of the method.

but they lie on smooth curves continuing those given. The lowest curve represents the beginning of curve K, magnified tenfold.

Let us consider first the group of the five uppermost curves. All these curves, of course, are slightly convex upward, because the coefficient of

expansion of water increases with the temperature; the greater the coefficient of expansion of water, the smaller is the rise of temperature necessary to counteract a given change in density due to added hydrochloric acid. The departure from a straight line is greater here than in the cases studied before. The lowest curve (I), representing soft glass, is steeper than the others, because the coefficient of expansion of soft glass is greater than that of the borosilicate glass. The difference in slope would obviously give a means of computing the difference in the coefficients of expansion. The other four curves are not far from parallel; thus the three varieties of borosilicate glass have approximately the same coefficients of expansion. Curves J and M both represent Jena reagent glass. They converge slightly toward the upper corner; a part of this convergence is due to the greater coefficient of expansion of water at the higher temperature, but this will not account for quite all of the effect. The two samples must therefore have differed slightly in coefficient of expansion. This is unfortunate, because it seems to indicate that each float must be standardized for itself; even a glass reputed to be of constant composition is not sufficiently definite to give precisely similar results with this very sensitive method, using different samples. Because of this limitation, it is hardly worth while to give equations of the type $n = at + bt^2 + ct^3$ for the curves, although if one wished to do much work with a single float this would be advantageous. The curves are to be regarded rather as typical than as universally applicable. Nevertheless, since the curvature is of necessity similar in the different cases, these curves may be of use to others in subdividing an interval when the two terminal temperatures are known, with any float of borosilicate glass.

The most obvious use for such curves, as previously stated, lies in the means which they afford of analyzing solutions with the help of a standardized thermometer. When no other more convenient means of analyzing the solutions exist, the method might be very useful in investigations demanding many determinations of the same type. Even if one has not a standardized thermometer at hand he can, nevertheless, use curves of this sort, provided that his thermometer is calibrated with reference to itself, or has an even bore; but of course in such a case his curves would correspond only to that particular thermometer.

The lowest curve in the diagram (Fig. 2) records the beginning of the curve with "Durobax" glass magnified tenfold; here the unit of the abscissa numbers represents a concentration of 0.1 g. per 1000 g. of solution. Because of the possibility that the increasing appearance of the hydroxyl ion at very great dilution may affect the curve,¹ more data

¹ Lamb and Lee have pointed out the remarkable effect of hydrolysis on very dilute sodium carbonate solutions. The possible effect referred to above is somewhat analogous (*loc. cit.*).

than those now presented will be required to fix this enlarged curve with complete accuracy at its lower left-hand corner, but it will serve for the present to exemplify the possible usefulness of the method with very dilute solutions. Such a single curve might be made applicable to many other substances besides hydrochloric acid, as follows:

In the first place, solutions of most substances as dilute as those covered by this curve must have very nearly the same coefficient of expansion as pure water. This inference is drawn from the data concerning the coefficients of expansion:¹ because it appears that the change in the coefficient of expansion of dilute aqueous solutions is nearly linear with the concentration, interpolation between concentrations of perhaps 1% and zero may be made with confidence; and one concludes that all solutions within this range must have a coefficient of expansion within a fraction of a per cent. of that of pure water. Hence this curve becomes not only a curve referring to hydrochloric acid alone, but also (within this range of error) to many other substances. The relation between different substances would thus become only a question of the density of the solution, and the curve would thus become a means of measuring density by means of the thermometer. Even if the hydrochloric acid has an irregularity at very great dilution, salt solutions from strong acids and bases have not (Lamb and Lee) and one of these would certainly serve if an acid would not. At this temperature a solution of hydrochloric acid which contains 0.1 g. of hydrochloric acid per 1000 g. has been found to have (again by interpolation between the almost linear larger concentrations and zero) a density almost exactly 0.000050 greater than pure water. To use the curve with any other specified substance one would need only to multiply the figures for hydrochloric acid by a proportional factor corresponding to the special salt. For example, one-tenth of a gram of sodium hydroxide per kilogram changes the density by 0.000115 or 2.30 times more than the same weight of hydrochloric acid. In order to reduce the figures as given for hydrochloric acid to those corresponding to sodium hydroxide, it would be, therefore, necessary only to divide them by 2.30. These figures are calculated from the known densities of the corresponding solutions as found by others. This extension of the method, now tentatively suggested as possible, deserves further trial and will be experimentally tested in the near future.

The manner of using curves of this sort for standardizing a thermometer has been already recorded in one of the previous papers.²

The present work has not yet brought any of this work to the stage of finality, but it confirms the conclusion of the previous papers that, because of the extreme sensitiveness of the indication of floating equi-

¹ For example, see Landolt and Börnstein, *Tabellen*, 1912, p. 338.

² THIS JOURNAL, 36, 9 (1914).

librium, the method may be one having many uses if the experimenter takes due precautions. Of course this method like many other phenomena concerning change of temperature cannot without great care, at least in its present stage, be depended upon to yield results as accurate as its readings are sensitive, chiefly because of the irregularities of the glass float. Anticipated work with a float of pure metal, which would be expected to be free from thermal hysteresis and would have a definite coefficient of expansion, has had to be postponed because of the difficulty of preparing such a float, but this task has been completed and in the future it is hoped such a float may be tested. Doubtless it would give more constant results than those described above.

We are glad to acknowledge our indebtedness to the Carnegie Institution for some of the apparatus used in this research.

Summary.

The solubility of paraffin in water has been examined and shown to be very small. For many purposes the use of paraffin-lined bottles as containers for standard solutions is, therefore, recommended.

Several newly described precautions, necessary for very exact work with floating bulbs in determining floating equilibrium, are recorded, and the effects of electrostatic charge, of varying pressure on liquid and float, and other possible causes of error were studied in detail.

The slow contraction of glass after fusion has been studied over a long range. This is a very important possible source of error in work of this kind, as suggested in the earlier papers.

Air dissolved in water at 20° has been shown to affect the density of water by less than 0.0000002.

Concentration-temperature curves have been studied with several floats made of different kinds of glass in dilute solutions of hydrochloric acid.

Such curves may be used for analyzing such hydrochloric acid with the help of similar floats and a standard thermometer, or for subdividing intervals of an uncalibrated thermometer. Until floats of perfectly definite composition are obtained, however, results for any one float cannot safely be used with another without preliminary testing on both ends of the range employed.

Because of the almost identical coefficients of expansion of very dilute solutions, the beginnings of such a curve may perhaps be used for many other solutions besides hydrochloric acid; it becomes a curve connecting approximately the density of any very dilute solution with the temperature of floating equilibrium. Thus one can determine densities thermometrically. The method will probably be more useful with such dilute solutions than with any others, but one must be on the lookout for the

change in the concentration of the hydroxyl ion in extreme dilutions of an acid.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS.]

SEPARATION OF THE METALS OF THE TIN GROUP.¹

By J. M. WELCH AND H. C. P. WEBER.

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The customary methods for the separation of arsenic, antimony and tin for qualitative purposes depend, in principle, either on the relative strength of the acids of these elements (for instance, the ammonium carbonate separation of arsenic from antimony and tin), or upon the difference in the solubilities of their sulfides in acids.² Of these principles the latter is perhaps the one most made use of in present practice.

Thus, in the procedure outlined by A. A. Noyes and W. Bray,³ the three elements are separated from each other by the use of graded concentrations of hydrochloric acid. In the hands of a practiced operator this method leaves little to be desired, and is one of the most satisfactory methods described. When, however, the method was employed by persons of less manipulative expertness, such as students entering for the first time into qualitative work, the results were by no means as satisfactory as might have been anticipated. The statistics collected⁴ show tin as giving the greatest trouble, it being missed in 20.2% of the cases considered. Arsenic was overlooked in 18% of the cases, while antimony was very rarely missed (less than 1%).

According to the method of Noyes, the sulfides of the second group are precipitated and then separated by treatment with ammonium polysulfide in much the usual manner, As_2S_5 , Sb_2S_5 and SnS_2 being thrown out from the resulting polysulfide filtrate upon acidification with hydrochloric acid. Up to this point no particular difficulty is encountered, except occasionally with copper, which dissolves to a slight extent in ammonium polysulfide. This will be referred to again under the description of the new procedure.

The precipitated tin group sulfides, superficially dried, are then treated with exactly 10 cc. of concentrated hydrochloric acid (sp. gr. 1.20), and warmed for 10 minutes on the steam bath. Arsenic sulfide remains

¹ Presented as thesis for the degree of B.S. by J. M. Welch to the College of Liberal Arts and Sciences, University of Illinois.

² A separation based upon the precipitation of antimony as the pyroantimonate of sodium has been proposed by Hahn, *Z. anorg. Chem.*, 92, 168 (1915).

³ *THIS JOURNAL*, 29, 137 (1907).

⁴ From reports of the students in qualitative analysis first semester 1914-1915. About 200 reports were examined.

behind, and antimony and tin go into solution as SbCl_3 and SnCl_4 , respectively.

Up to this point the method here proposed follows the lines laid out by Noyes and Bray,¹ but from here on the procedure is modified. In the original method the filtrate containing the antimony and tin is diluted so that 50 cc. of solution contain 10 cc. of concentrated hydrochloric acid. Hydrogen sulfide is then passed into the solution, *which meanwhile should be kept at 90°*. If no precipitate is formed, further 5 cc. of water are added and hydrogen sulfide is again passed into the solution. If antimony sulfide has been formed it is removed by filtration, the tin is then precipitated as the sulfide from the cold solution, after dilution to 70 cc.

If these steps are carried out with proper attention to the essential details the results are very satisfactory. The limits of dilution are not very wide, however, and in addition the temperature must be controlled. Errors at this point of the procedure will cause the formation of a "brown precipitate," as has been noted by Noyes and Bray. As a matter of experience, this error was a very common one on the part of numerous students using the method. Aside from the fact that the characteristic color of antimony sulfide is masked, producing corresponding uncertainty in the interpretation of the results, large quantities of tin are lost with the antimony. Unless the precipitate is again treated by a special procedure, tin may be, and often is, overlooked entirely.

Experimental.

In the literature very little is to be found concerning the nature of the brown precipitate formed when antimony and tin sulfides are precipitated together. Its color in no way corresponds to that of a mixture of the two sulfides, and in view of the regularity and ease with which it is formed it is strange that so little mention is made of it. Of the well-known texts on qualitative analysis, that of A. A. Noyes, and one or two others, are the only ones which mention it. No reference is found in the general literature. Pouget² has described a number of compounds which are possibly of the same nature. By precipitating salts of the metals with solutions containing K_3SbS_5 he obtained compounds of the type Me_3SbS_5 and Me_3KSbS_5 . For the heavy metals, these are brown to black precipitates of constant composition. The alkali-earth compounds are white to yellow, the manganese salt is rose colored. The mineral pyrargyrite, Ag_3SbS_4 , is a naturally occurring example of these thioantimonites. The tin thioantimonite has not been described.

It is possible that the brown precipitate is of the same general character as the compounds described by Pouget. It is formed whenever

¹ *Loc. cit.*

² *Compt. rend.*, 124, 1445, 1518 (1897); 126, 1144, 1792 (1898); 129, 103 (1898).

tin and antimony sulfides are precipitated together from a dilute hydrochloric acid solution. When equivalent portions of nearly neutral solutions of sodium thioantimonite and stannic chloride are mixed (molar solutions), a muddy black precipitate is formed at once, which darkens on standing. With excess of antimony the color is shifted somewhat to the red, while with corresponding excess of tin the yellow predominates more and more. Occasionally, when much antimony is present, its sulfide may be observed to form first on passing hydrogen sulfide into the solution and as the precipitation proceeds the characteristic drab-colored compound is formed. The preparation of a definite tin thioantimonite has so far not been undertaken, but the characteristic way in which such solutions reacted led to an investigation of the reliability of the behavior as an indication of tin and antimony.

In order to determine the limits between which this substance would reveal its presence, varying quantities of stannic tin and trivalent antimony were mixed and diluted to 70 cc., with an acid content of 10 cc. of hydrochloric acid. These solutions were then precipitated at ordinary temperatures by means of hydrogen sulfide. The relative concentrations of the two metals in the test solutions are given in Table I.

TABLE I.

Composition of Solutions for the Investigation of the "Brown Precipitate."

Solution.	Sb per cc. (mg.).	Sn per cc. (mg.).	Ratio. Sb/Sn.	Solution.	Sb per cc. (mg.).	Sn per cc. (mg.).	Ratio. Sb/Sn.
A.....	6.30	0.32	20/1	N.....	2.24	1.28	7/4
B.....	5.98	0.32	19/1	O.....	1.92	1.60	6/5
C.....	5.66	0.32	18/1	P.....	1.60	1.92	5/6
D.....	5.34	0.32	17/1	Q.....	1.28	2.24	4/7
E.....	5.02	0.32	16/1	R.....	0.96	2.56	3/8
F.....	4.70	0.32	15/1	S.....	0.64	2.88	2/9
G.....	4.38	0.32	14/1	T.....	0.32	3.20	1/10
H.....	4.06	0.32	13/1	U.....	0.32	3.52	1/11
I.....	3.74	0.32	12/1	V.....	0.32	3.74	1/12
J.....	3.52	0.32	11/1	W.....	0.32	4.06	1/13
K.....	3.20	0.32	10/1	X.....	0.32	4.38	1/14
L.....	2.88	0.64	9/2	Y.....	0.32	4.70	1/15
M.....	2.56	0.96	8/3				

Solutions "A" to "K" gave red to red-brown precipitates, "K" to "S" were decidedly brown, while the precipitates from solutions "R" to "Y" varied from clay-brown to yellow-brown.

With the ratio of the antimony content to the tin content varying as given in solutions "I" to "U" the brown color was easily recognized, being most sharply defined in the region indicated by solutions "K" to "S," inclusive. When the antimony was present in greater proportion than is indicated in "I," it was difficult to discover a marked difference between the color of the precipitate and that of a precipitate of antimony

sulfide alone. When the proportion of the tin exceeded that given in solution "U" the yellow color of tin sulfide predominated, so that there could be no doubt as to its presence. The presence of antimony was indicated under these conditions by the red precipitate first formed when hydrogen sulfide was passed into the solution.

It was found that, within the limits indicated, not only was the characteristic brown precipitate obtained, but also that a colorimetric estimate of the relative proportions of the two constituents, tin and antimony, was possible. In order to show this the precipitates listed in Table I were renumbered so as not to suggest their composition and beginners from the laboratory were asked to arrange them in the order of the color gradations from red through brown to yellow. This was repeated a number of times and in every case the precipitates from "K" to "S," inclusive, were arranged in the order of decreasing antimony-tin ratio.

From this it would appear that when the ratio of antimony and tin in a mixture lies between $12/1$ and $1/12$, the color of the precipitate formed by the action of hydrogen sulfide in a solution containing the equivalent of 10 cc. of concentrated hydrochloric acid to a volume of 70 cc. is a very valuable indication of the presence of tin.

Treatment of the Precipitate.—If a separation of the antimony and tin is not desired, the precipitate is ready for the procedure devised by Pertusi and Gastaldi.¹ According to this method the sulfides are suspended in a little water and shaken with metallic magnesium powder. The tin compound is reduced to the metal and is after reduction dissolved in dilute hydrochloric acid. The solution is allowed to run through a filter into mercuric chloride solution, the SnCl_2 revealing its presence by the production of mercurous chloride. The antimony does not interfere with the reaction, and in the case of all mixtures listed in Table I satisfactory tests were obtained for tin by this method. No particular account is taken of antimony in this process, however, and it seemed advisable to include a positive confirmation of this element in the steps taken, particularly to take care of the extreme mixtures where antimony or tin predominates very largely.

One of the most satisfactory tin and antimony separations is that of F. W. Clarke,² which is used for the quantitative separation of these two elements. A series of tests of this method was made, for the purpose directly in view, with solutions similar to those given in Table I. In these the proportion of antimony to tin ranged from $20/1$ to $1/20$, and in every instance both elements were recognized without difficulty. The conditions of the separation are that the combined weight of the two

¹ *Rend. soc. chim. ital.*, 4, 83 (1914).

² *Chem. News*, 21, 124 (1870).

metals shall not exceed 0.3 g., that for each 0.1 g. there should be present 5 g. of oxalic acid, and that the tin should be in the stannic form. These conditions are readily met in the ordinary qualitative separation.

In the separation, as ordinarily carried out, H_2S is passed into the hot oxalic acid solution. Antimony sulfide precipitates, of characteristic color and easily filtered, and tin remains in solution. A reversal of the steps was examined for its usefulness, but was found unsatisfactory. It is not possible to achieve a sharp separation of antimony and tin by boiling the mixed sulfides with an oxalic acid solution. Either the tin does not completely dissolve or some of the antimony dissolves with it. It was therefore found necessary to dissolve the antimony-tin mixture completely and then to precipitate the antimony alone. The steps as finally devised will be described under the procedure.

Procedure.

To the precipitated sulfides from the ammonium sulfide separation, after having dried them superficially either by suction or by pressing between filter paper, add exactly 10 cc. of concentrated hydrochloric acid (sp. gr. 1.20) and heat for ten minutes on the steam bath. Arsenic sulfide remains behind and is removed by filtration and examined in the customary manner.

It is assumed that the ammonium sulfide separation from the copper group has been sharp and that neither mercury nor copper is present in this portion of the material. It often occurs that copper dissolves in the ammonium polysulfide (which shows itself in the brown color of the solution). Sodium sulfide does not present this difficulty, but it dissolves mercuric sulfide. If ammonium polysulfide, to which about 5% of NaOH has been added, is used, both difficulties are avoided and a reagent of striking superiority over ammonium polysulfide alone is obtained. To show this, the following mixtures were precipitated: two test tubes each with milligram-mols of mercury, tin and antimony; two, each with milligram-mols of copper, antimony and tin. The precipitates were washed by decantation, and to one of the mercury precipitates and to one of the copper precipitates ammonium polysulfide, containing 5% of NaOH, was added. To the other two precipitates ammonium polysulfide without NaOH was added. All four test tubes were placed in boiling water. The tin group sulfides dissolved immediately in the solvents containing NaOH, and in three minutes the contents of the two tubes consisted of a clear golden yellow solution free from copper or mercury, and a jet-black, dense precipitate of the copper group sulfide at the bottom of the tube. In the comparison tubes, on the other hand, the tin group had not, under the same conditions, dissolved completely after three hours and, furthermore, the ammonium polysulfide had dissolved an appreciable amount of copper.

The filtrate from the arsenic, which contains antimony trichloride and tin tetrachloride, is diluted to a volume of 70 cc. and is saturated with H_2S . If the addition of the H_2S takes place while the solution is hot, a portion of the antimony will precipitate first as the red sulfide, but on further addition of H_2S , and as the solution cools, a brown to nearly

black precipitate is formed, which is characteristic of tin plus antimony. With practice, the intensity of the coloration may be made the basis of an estimate of the relative quantities of the two constituents. As soon as the formation of this precipitate is observed, the introduction of H_2S is interrupted and the solution and precipitate are heated again until the excess of H_2S is driven off. Five cubic centimeters of hydrogen peroxide solution (3%) are added and the solution is heated until the precipitate has redissolved. Five to ten grams of oxalic acid are now added and H_2S is again passed into the hot solution, which is allowed to cool while it is being saturated. Antimony sulfide precipitates as a bright red, easily filtered precipitate, and is then collected on the filter.

The mixed precipitate may be redissolved by simply evaporating the solution with the precipitate. Upon addition of H_2O_2 the same end is attained without evaporation and in much shorter time. A few drops of bromine water are still more effective in this respect. The excess H_2S is best driven off before adding these oxidizing agents. A large excess should of course not be used, since it would decompose the oxalic acid added later. As antimony sulfide is to be precipitated at the next step, it is not necessary to wait for the last faint red cloud of antimony sulfide to redissolve at this part of the procedure.

The filtrate from the antimony sulfide, which contains the tin, or a portion of the filtrate (10 cc. is usually sufficient), is boiled with 1-2 g. of granulated test lead for two or three minutes. The solution is then chilled (by running water), and filtered into a solution of mercuric chloride. In the presence of tin, white mercurous chloride is formed.

The solution contains tin in the tetravalent state. Upon boiling this with metallic lead this is reduced to stannous tin, which gives the well-known reaction with mercuric chloride. Trials in connection with the method showed that it was reliable with as little as 0.5 mg. of tin. Some of the lead goes into solution during the heating and crystallizes out again upon cooling (as lead chloride). While this precipitate is different in character from the mercurous chloride, errors are avoided by cooling the solution first and filtering from the lead salt.

Summary.

1. It has been shown that when antimony and tin are precipitated together, as sulfides, they form a characteristic brown precipitate (which is possibly a sulfantimonite of tin). Within rather wide limits this is a reliable indication of the presence of these two elements.
2. It was found that the reduction of stannic compounds to stannous compounds by means of metallic lead could be carried out with sufficient ease and accuracy to make it available as a method for the detection of tin.
3. A method for the qualitative analysis of the tin group has been described, which has proven effective in use, particularly in the hands of inexperienced students, and which, it is believed, has some advantages in latitude of conditions, speed, and ease of manipulation.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

A SUPPOSED EFFECT OF THE FORM OF CONTAINER UPON THE DENSITY OF A GAS.

BY WILLIAM A. NOYES AND LAURENCE C. JOHNSON.

Received March 28, 1916.

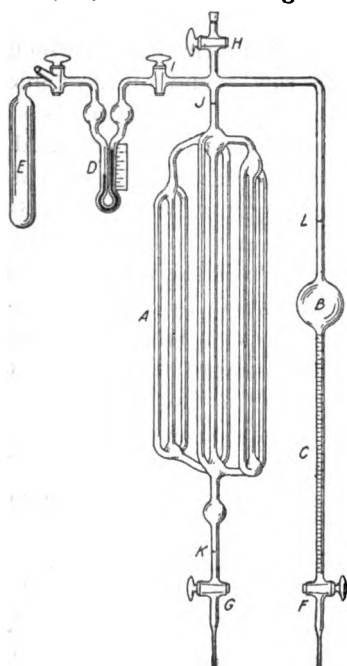
From his first series of determinations of the volumetric ratio in which oxygen and hydrogen combine to form water, Morley¹ found a mean value of 1 : 2.00023, the volumes being calculated to standard conditions of temperature and pressure. In his experiments the gases were measured, saturated with water vapor, in a eudiometer tube which was enclosed in a water jacket. Scott,² a few years later, reported the value 1 : 2.00285 for this ratio, the gases being measured moist but in a spherical vessel. In neither of these cases does the "probable error" of the mean exceed one part in twenty-five thousand. The value found by Scott agrees with the value which may be calculated from Morley's later results on the atomic ratio of oxygen and hydrogen, taken together with his value for the ratio of the densities of the two gases. In Morley's determination of the densities the gases were dried and measured in globes. The difference between the values obtained by Scott and by Morley is equal to one part in one thousand, or twenty-five times the value of the "probable error" in either determination.

In attempting to account for the discrepancy in these values, Morley³ suggests that the shape of the vessel may, in some way, be responsible, the effect being due to the attraction upon the gas, either of the walls of the container or of the water surrounding the vessel. Assuming this explanation to be correct, the effect of the shape of the containing vessel as measured in the ratio of the combining volumes is a differential one, and the effect should manifest itself in the case of at least one of the gases. In other words, if the gas is measured in a tube, then transferred to a bulb, and placed under the same temperature and pressure, the volume occupied by the gas in the bulb would differ from that which it occupied in a tube, and this difference would amount, in the case of one of the gases, to at least one part in a thousand.

We have devised an apparatus to measure the volume of a certain quantity of gas contained in a system of tubes as compared with the volume occupied by the same quantity of gas when contained in a bulb. The tube system A (see figure) consists of nine tubes having a total length of about 470 cm. and an average internal diameter of 6.6 mm. To the lower side of the bulb B, which has about the same capacity as the system

¹ *Am. J. Sci.*, 41, 220 (1891).² *Phil. Trans.*, (A) 184, 543 (1893).³ "On the Densities of Oxygen and Hydrogen, etc.," Smithsonian Institution, 1895, p. 82.

of tubes, is fused a graduated tube of small internal diameter, C. The two systems are connected by capillary tubing, which also connects a sulfuric acid manometer, D, on the other side of which is an elongated bulb, E, made from large-sized tubing. The volume of this bulb is ap-



proximately the same as either the tube system A or the bulb B. The volume of the tube was defined by two scratches in the capillary tubing J and K, one above and one below the enlarged portion. The volume of the bulb system was defined at the top by a scratch on the capillary L, the lower limit being variable through the length of the graduated tube. Thus, after careful calibration it was possible to determine the point on the graduated tube which should limit the volume of the bulb system to make it just equal that of the tube system.

The volume of each of the two systems was determined by filling with mercury, then weighing the amount which had to be drawn off in order to lower the level to the lower mark. To make sure that there was no error in the determination of the volume due to a distortion of the glass by

the weight of the mercury, the calibration was also made with water. To accomplish this the capillary leading to the manometer was cut so as to permit the apparatus being suspended from the beam of a large balance, from which the front and rear doors had been removed. The errors in the determination of the volume by this method were much larger than when mercury was used, but the results serve to show that there is very little, if any, distortion by the mercury.

The method of comparing the volume occupied by a gas in the two systems was as follows: After the entire apparatus had been filled with the gas to be measured, the mercury was admitted through F until the bulb system was filled, and through G until it reached the lower mark of the tube system. The stopcock H was then closed and the height of the sulfuric acid noted by means of a small scale attached to the manometer which was read by means of a cathetometer. The mercury was then allowed to rise in the tube system until it reached the upper mark and the mercury in the bulb system was allowed to fall until it reached a point in the calibrated tube nearly corresponding to the volume of the tube system. The manometer was then read and the mercury set at another

point in the graduated tube and the manometer again read. From these two readings a simple interpolation gave the point at which the mercury should have been set to give the pressure initially present in the tube system. The gas was immediately returned to the tube system and the manometer again read. In case this reading indicated a decided change in pressure the measurement was discarded, but if only a small change was noted the mean of the two readings was taken for the interpolation. A change in pressure between the first and second readings in the tube system indicated, of course, a relative change in temperature between the tube system and the bulb E which would vitiate the result.

For the first series of measurements the entire apparatus, with the exception of the leveling bulbs, was enclosed in a box with a glass door. The case also contained a motor-driven fan which provided a rapid circulation of air. Thus while it was not possible to maintain a constant temperature during the transfer of the gas, the results were not affected, since the temperature of E changed with that of the bulb and tube system. Four series were run, air and hydrogen both being used dry as well as saturated with water vapor. While slight differences in volume were noted in the two systems the largest mean is less than one part in ten thousand, which is the order of our experimental error and could not explain the disagreement referred to above.

Following a suggestion of Professor Morley¹ that the abnormality might be due to the attraction of the water which surrounded his eudiometer tube, we enclosed both our systems in a water jacket. This was made of wood, with glass front and back, the bottom being made in two parts to allow the setting in place of the glass apparatus. For setting the glass, as well as making the other joints water tight, we found a mixture of equal parts of rubber and rosin, melted together, very satisfactory. Where greater strength is required the amount of rubber is decreased. The box when finished had a capacity of about twenty liters, so that when filled with water it could be maintained at a very constant temperature. The bulb E was also surrounded with water contained in a two-liter Dewar flask. As would be expected, the individual determinations do not vary as far from the mean as in the first series. It may be seen from the results of this series that any difference in volume which may be indicated is not larger than one part in 20,000. The small differences in volume which are shown by the results may be due to small bubbles of air which remained between the mercury and the glass when the level of the former was raised, and which were so small or so placed as to escape detection. The gases used were not carefully purified as it was assumed that the small amounts of impurities which might be present would have no bearing on the effect which we were attempting to measure.

¹ Private communication.

Experimental.**CALIBRATION OF THE TWO SYSTEMS, VOLUMES CALCULATED TO 20°.**

Tube system measured with water.		Tube system measured with mercury.	
178.498 cc.		178.509 cc.	
178.515		178.511	
178.507			
<hr/>		<hr/>	
Mean,	178.507 cc.	Mean,	178.510 cc.
Bulb system measured with water to calibration 0.400.		Bulb system measured with mercury to calibration 0.400.	Bulb system measured with mercury to calibration 1.638.
178.115 cc.		178.119 cc.	179.378 cc.
178.128	Volume to zero	Volume to zero	
	on scale,	on scale,	
	177.719 cc.		177.720 cc.
Mean,	178.121 cc.		

The tube system was accidentally broken before the last two sets of determinations had been made, which necessitated a new calibration of this part after the apparatus had been repaired. This was done with mercury and gave the value 178.586 cc.

COMPARISON OF VOLUMES, APPARATUS IN AIR.

Dry Air.			Dry Hydrogen.		
Vol. in tubes.	Vol. in bulb.	Diff.	Vol. in tubes.	Vol. in bulb.	Diff.
178.510 cc.	178.507 cc.	-0.003 cc.	178.510 cc.	178.492 cc.	-0.018 cc.
	178.503	-0.007		178.505	-0.005
	178.500	-0.010		178.500	-0.010
	178.501	-0.009		178.494	-0.016
	178.506	-0.004		178.490	-0.020
	178.501	-0.009		178.519	+0.009
	178.490	-0.020		178.513	+0.003
	178.515	+0.005		178.513	+0.003
	178.002	-0.008		178.505	-0.005
	178.515	+0.005		178.502	+0.008
<hr/>			<hr/>		
Mean,	178.504 cc.	-0.006 cc.	Mean,	178.503 cc.	-0.007 cc.
Air, Saturated with Water Vapor.			Hydrogen, Saturated with Water Vapor.		
Vol. in tubes.	Vol. in bulb.	Diff.	Vol. in tubes.	Vol. in bulb.	Diff.
178.510 cc.	178.508 cc.	-0.002 cc.	178.510 cc.	178.508 cc.	-0.002 cc.
	178.496	-0.014		178.498	-0.012
	178.488	-0.022		178.506	-0.004
	178.489	-0.021		178.492	-0.018
	178.506	-0.004		178.505	-0.005
	178.484	-0.026		178.498	-0.012
	178.494	-0.016		178.494	-0.016
	178.496	-0.014			
	178.512	+0.002			
<hr/>			<hr/>		
Mean,	178.497 cc.	-0.013 cc.	Mean,	178.500 cc.	-0.010 cc.

DETERMINATIONS WITH APPARATUS IN WATER BATH.

Gas, Dry Oxygen.			Dry Hydrogen.		
Vol. in tubes.	Vol. in bulb.	Diff.	Vol. in tubes.	Vol. in bulb.	Diff.
178.510 cc.	178.509 cc.	—0.001 cc.	178.510 cc.	178.509 cc.	—0.001 cc.
	178.507	—0.003		178.514	+0.004
	178.515	+0.005		178.523	+0.013
	178.511	+0.001		178.518	+0.008
	178.518	+0.008		178.520	+0.010
	178.512	+0.002		178.518	+0.008
<hr/>			<hr/>		
Mean,	178.512 cc.	+0.002 cc.	Mean,	178.517 cc.	+0.007 cc.
Oxygen, Saturated with Water Vapor.			Hydrogen, Saturated with Water Vapor.		
Vol. in tubes.	Vol. in bulb.	Diff.	Vol. in tubes.	Vol. in bulb.	Diff.
178.586 cc.	178.599 cc.	+0.013 cc.	178.586 cc.	178.594 cc.	+0.008 cc.
	178.591	+0.005		178.595	+0.009
	178.586	+0.000		178.601	+0.015
	178.597	+0.011		178.585	—0.001
	178.590	+0.004		178.599	+0.013
<hr/>			<hr/>		
Mean,	178.592 cc.	+0.006 cc.	Mean,	178.593 cc.	+0.007 cc.

Summary.

We have compared the volume occupied by a gas in a system of tubes with that which it occupies in a bulb, in an effort to explain the difference in the volumetric ratio of hydrogen to oxygen in water as determined by Morley and by Scott. We have shown that there is no difference in volume larger than one part in ten thousand, whereas the two determinations referred to differ by one part in one thousand.

URBANA, ILL.

THE DENSITY OF AQUEOUS SOLUTIONS OF COPPER SULFATE AND SULFURIC ACID.

BY H. D. HOLLER AND E. L. PEPPER.¹

Received March 25, 1916.

I. INTRODUCTION.

In connection with an investigation on the regulation of solutions for electrodeposition, especially of acid copper sulfate solutions for electrotyping, it was found desirable to devise a simple method of determining and adjusting their composition. Since the solutions usually employed for the above purpose contain only copper sulfate and sulfuric acid, the composition of any given solution is fixed if the acid content and density at a given temperature are known. The density can be readily determined with a hydrometer, and the acidity can be ascertained with sufficient

¹ Published by permission of the Director of the Bureau of Standards.

accuracy by titration with standard alkali, using methyl orange as indicator, as described by Wogrinz.¹ In order, therefore, to learn the content of copper sulfate, all that is required is a table showing the density of solutions containing known amounts of copper sulfate and of sulfuric acid.

Although the densities of solutions of copper sulfate and of sulfuric acid have been determined separately, no systematic study of the densities of solutions containing both could be found in the literature. Only in isolated cases were such data given concerning certain baths, such as those recommended by Pfanhauser,² Langbein-Brannt,³ Steinach and Buchner,⁴ and others.

The concentration of solutions containing both copper sulfate and sulfuric acid is limited by the fact that addition of sulfuric acid to copper sulfate solution causes a marked decrease in the solubility of the copper sulfate. Thus, while 395 g. of crystallized copper sulfate is contained in 1 liter of the saturated solution at 15° the addition of 100 g. per liter of sulfuric acid reduces the solubility of the copper sulfate to 215 g. per liter. Since in any practical work it is necessary to use solutions somewhat removed from the saturation point, the actual field is probably included in the range of 0 to 20% of each of the constituents. Such solutions, therefore, formed the basis of this investigation. The temperature range of 25° to 40° was selected as including the normal temperature employed in most copper plating or refining operations. Doubtless the expansion coefficients determined from such data will permit extrapolation over a moderate range above and below the temperature used.

II. METHOD OF INVESTIGATION.

1. Preparation of Solutions.

In order to avoid the influence of temperature in the preparation of the solutions, they were all made of a known composition by weight, expressed in g. of each constituent per kg. of solution. They were prepared in duplicate by mixing accurately weighed portions of water and of standardized concentrated solutions of copper sulfate and of sulfuric acid.

The stock sulfuric acid solution was prepared by diluting C. P. acid to about 12 normal with distilled water, and was standardized by the barium sulfate method with the usual precautions. It was also compared with a hydrochloric acid solution, standardized by silver chloride precipitation, through a solution of sodium hydroxide, using methyl orange as indicator.

The concentration of the sulfuric acid solution as determined by the barium sulfate method agreed with that obtained by comparison with the

¹ *Chem. Ztg.*, 37, 869 (1913).

² "Die Galvanoplastik," 1904, p. 37-38.

³ "Electrodeposition of Metals," 7th ed., 1913, p. 574-575, 590.

⁴ "Die Galvanische Metallniederschläge," 1911, p. 160-161.

standard hydrochloric acid solution to within about 1 part in 1500. Weight burets were used, the individual titrations agreeing to within less than 1 part in 2000.

The solution of copper sulfate was prepared from recrystallized salt, which gave a perfectly clear solution. The concentration of copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was calculated from the copper content determined electrolytically, the greatest difference between any two results being 1 part in 3000. Complete removal of copper from the electrolyte was confirmed by testing with $\text{K}_4\text{Fe}(\text{CN})_6$.

2. Density Determination.

Method of Determination.—The density measurements were made by the method of hydrostatic weighing, *i. e.*, by weighing in the sample under investigation a sinker of known mass and volume. The density¹ of the liquid is then calculated by means of the equation

$$D_t = \frac{W - \frac{(w - w_1) + (w - w_2)}{2} \left(1 - \frac{\rho}{8.4}\right)}{V_t}$$

in which

D_t = Density at temp. t

W = Mass of sinker *in vacuo*

w = Weighings with sinker off

w_1 and w_2 = Weighings with sinker on

ρ = Air density

8.4 = Assumed density of brass weights

V_t = Volume of sinker at temp. t

Apparatus Used.—The apparatus used is described in detail in Bureau publications.² A short description of the apparatus is given as follows:

The densimeter tube (about 45 cm. long and 2.5 cm. in diameter) containing the sample is placed in a water bath which is kept in constant circulation. This bath is surrounded by another, also in circulation, the temperature of which is regulated by means of an electric heating coil and a brine cooling coil. The temperature of the inner bath is determined by the use of two mercury thermometers. The large sinker having a length of approximately 33 cm. and diameter of 1.3 cm. is attached below a small sinker and both are suspended by means of a wire from one arm of a sensitive balance. The small sinker which is in the liquid at all times serves the purpose of keeping the suspension wire taut and in position, and thus the effect of surface tension is eliminated.

¹ Throughout this paper the term "density" is used to denote mass per unit volume and is here expressed in grams per milliliter. The densities are therefore numerically the same as specific gravities in terms of water at 4° as unity.

² *Technologic Paper No. 9* (1912) and *Bureau of Standards Bull.* 9, 371-378 (1913).

Method of Making Observations.—After sufficient time has elapsed for attaining temperature equilibrium at the desired temperature, the first weighing is made with the large sinker attached and the temperature is immediately read from each of the thermometers. Then the second weighing is made with the large sinker detached from the small sinker. In order to obviate any correction for a possible change in temperature the first weighing is repeated and the thermometers re-read. The average of the temperatures at the two weighings is taken as the true temperature. The difference between the mean of these two weighings and the second weighing is the apparent weight of the large sinker in the sample at the given temperature. After completing the observations at one point, the temperature is changed to the next and the process is repeated in the same order.

III. RESULTS OF INVESTIGATION.

The results of the density determinations and composition of the samples are shown in Table I.

TABLE I.
Density of Copper Sulfate—Sulfuric Acid Solutions.

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, g./kg.	CuSO_4 , g./kg.	H_2SO_4 , g./kg.	Density, ¹ 25°.	Mean density, 25°.	Density, 40°.	Mean density, 40°.	α , ²
50	31.97	0	1.03014	1.03016	1.02489	1.02488	—0.00035
50	31.97	0	1.03017		1.02488		
50	31.97	50	1.06297	1.06303	1.05637	1.05638	—0.00044
50	31.97	50	1.06309		1.05639		
50	31.97	100	1.09843	1.09843	1.09060	1.09060	—0.00052
50	31.97	100	1.09843		1.09060		
50	31.97	150	1.13552	1.13549	1.12669	1.12668	—0.00059
50	31.97	150	1.13546		1.12667		
50	31.97	200	1.17421	1.17416	1.16453	1.16452	—0.00064
50	31.97	200	1.17412		1.16452		
100	63.94	0	1.06454	1.06455	1.05871	1.05872	—0.00039
100	63.94	0	1.06456		1.05874		
100	63.94	50	1.09835	1.09834	1.09097	1.09097	—0.00049
100	63.94	50	1.09833		1.09097		
100	63.94	100	1.13497	1.13498	1.12642	1.12649	—0.00057
100	63.94	100	1.13499		1.12656		
100	63.94	150	1.17367	1.17366	1.16417	1.16418	—0.00063
100	63.94	150	1.17366		1.16420		
100	63.94	200	1.21399	1.21397	1.20379	1.20375	—0.00068
100	63.94	200	1.21395		1.20371		
150	95.91	0	1.10062	1.10063	1.09428	1.09430	—0.00042
150	95.91	0	1.10064		1.09431		
150	95.91	50	1.13555	1.13554	1.12765	1.12764	—0.00053
150	95.91	50	1.13553		1.12764		

¹ All densities here tabulated are expressed in grams per milliliter.

² Change in density per degree rise in temperature.

TABLE I (continued).

CuSO ₄ .5H ₂ O, g./kg.	CuSO ₄ , g./kg.	H ₂ SO ₄ , g./kg.	Density, 25°.	Mean density, 25°.	Density, 40°.	Mean density, 40°.	α .
150	95.91	100	1.17366	1.17364	1.16457	1.16455	-0.00061
150	95.91	100	1.17361		1.16453		
150	95.91	150	1.21392	1.21393	1.20391	1.20394	-0.00067
150	95.91	150	1.21394		1.20396		
150	95.91	200	1.24528	1.24523	...
150	95.91	200	1		1.24518		
200	127.9	0	1.13833	1.13834	1.13152	1.13153	-0.00045
200	127.9	0	1.13835		1.13154		
200	127.9	50	1	1.17485	...	1.16638	-0.00056
200	127.9	50	1.17485		1.16638		
200	127.9	100	1.21449	1.21448	1.20476	1.20476	-0.00065
200	127.9	100	1.21447		1.20475		
200	127.9	150	1.24579	1.24575	...
200	127.9	150	1		1.24571		

In Table I the composition of the solutions is expressed in g. of CuSO₄.5H₂O per kg. of solution. The concentration in g. per liter may be readily

TABLE II.

Showing the Relation Between Total Concentration and Density.

Total concentration, g./kg.	CuSO ₄ .5H ₂ O, g./kg.	H ₂ SO ₄ , g./kg.	Density, 25°.
50	0	50	1.0300
	50	0	1.0302
	100	0	1.0640
100	0	100	1.0640
	50	50	1.0630
	100	0	1.0646
	150	0	1.0994
150	0	150	1.0994
	50	100	1.0984
	100	50	1.0983
	150	0	1.1006
	200	0	1.1365
200	0	200	1.1365
	50	150	1.1355
	100	100	1.1350
	150	50	1.1355
	200	0	1.1383
250	0	250	1.1751
	50	200	1.1742
	100	150	1.1737
	150	100	1.1736
	200	50	1.1749
	300	0	1.2150
300	0	300	1.2150
	100	200	1.2140
	150	150	1.2139
	200	100	1.2145

¹ Solutions of these compositions do not exist at 25°.

² Sample lost by breakage of the container.

obtained by multiplying the above concentrations in g. per kg. by the corresponding densities. In each case density determinations were made upon duplicate solutions, and these results are seen to agree in most cases to somewhat better than 1 in the fourth decimal place. From the density data for 25° and 40°, respectively, the thermal density coefficient α has been calculated, which may be defined as the change in density (always negative) for an increase in temperature of 1°.

The above results are shown graphically in Fig. 1, which illustrates the

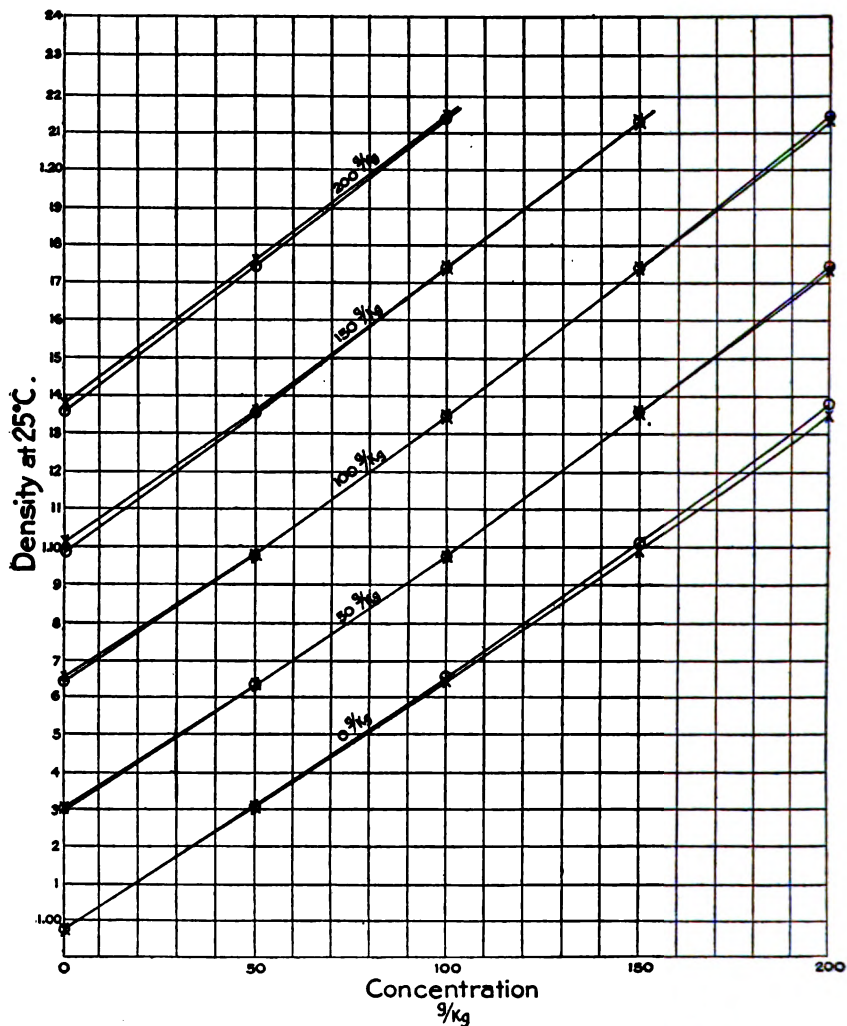


Fig. 1.—Density of copper sulphate-sulphuric acid solutions.

O — sulphuric acid constant.

X — copper sulphate constant.

effect upon the density of additions of copper sulfate to sulfuric acid solutions and of sulfuric acid to copper sulfate solutions. The curves for sulfuric acid solutions are derived from the data of Donke as given in Landolt and Börnstein, fourth edition (1912). The close agreement between the densities of solutions of the same total concentration, shown in Table II is illustrated in Fig. 1. The curves passing through the circles show the change in density produced by the addition of copper sulfate to solutions containing a definite amount of sulfuric acid per kg. of solution. Those through the crosses show the change in density produced by the addition of sulfuric acid to solutions containing a definite amount of copper sulfate per kg. of solution, the total concentration in each case being the same as for the corresponding curve through the circles.

Example.—In the case of the curves marked 50 g./kg., the one passing through the circles shows the change in density produced by the addition of definite amounts (50, 100, 150, 200 g.) of copper sulfate to a solution containing 50 g. of sulfuric acid per kg. of solution, and the one passing

TABLE III.
Total Concentration of Solutions of Given Density.

25° C.			40° C.		
Density.	CuSO ₄ ·5H ₂ O + H ₂ SO ₄ g./l.		Density.	CuSO ₄ ·5H ₂ O + H ₂ SO ₄ g./l.	
1.01	20		1.01	26	
1.02	36		1.02	43	
1.03	52		1.03	60	
1.04	68		1.04	76	
1.05	84		1.05	93	
1.06	100		1.06	110	
1.07	117		1.07	127	
1.08	133		1.08	144	
1.09	150		1.09	161	
1.10	166		1.10	178	
1.11	183		1.11	195	
1.12	200		1.12	212	
1.13	217		1.13	229	
1.14	234		1.14	247	
1.15	251		1.15	265	
1.16	268		1.16	282	
1.17	286		1.17	300	
1.18	303		1.18	318	
1.19	321		1.19	336	
1.20	339		1.20	354	
1.21	357		1.21	372	
1.22	375		1.22	390	
1.23	393		1.23	408	
			1.24	427	

through the crosses shows the change in density produced by the addition of the same definite amounts of sulfuric acid to a solution containing 50 g. of copper sulfate per kg. of solution.

From the above tables and curves it may be seen that:

1. Within the range studied, the density of copper sulfate-sulfuric acid solutions is approximately a linear function of the concentration.
2. The density of solutions of equal (not equivalent) concentrations of copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and of sulfuric acid is nearly identical.

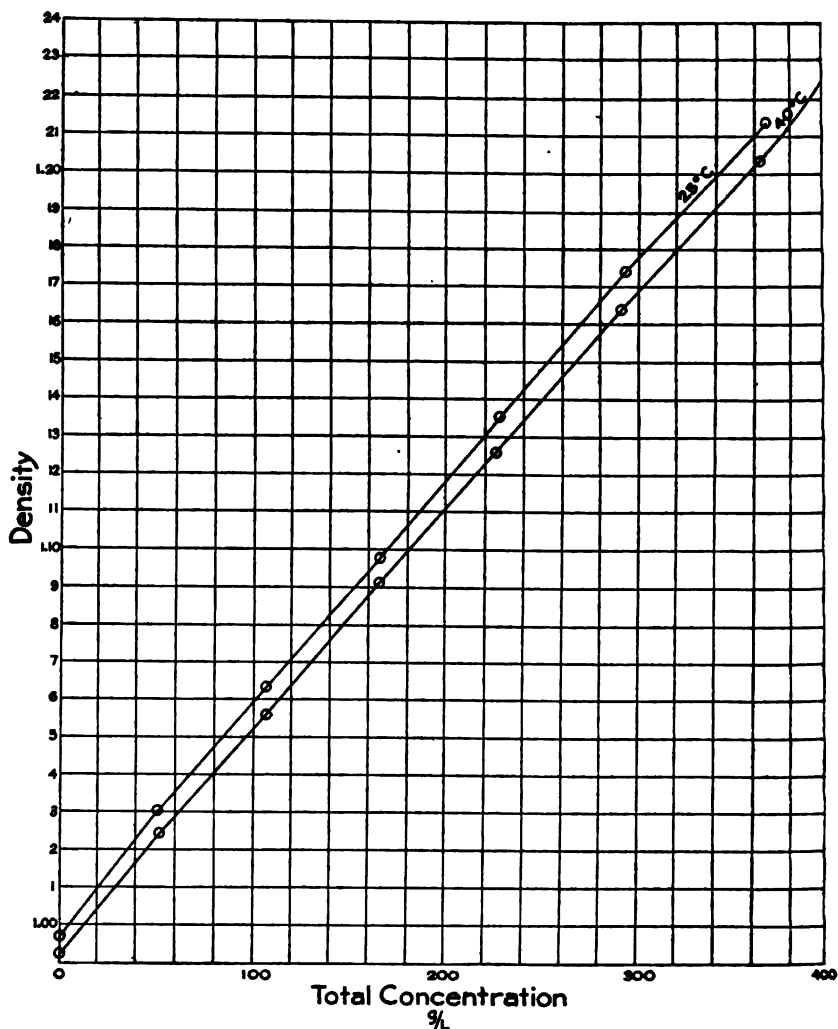


Fig. 2.—Density of solutions of total concentration of copper sulphate plus sulphuric acid.

3. As a natural consequence of the conclusions noted in (1) and (2), a curious relation was found to exist, *i. e.*, that the density of solutions containing appreciable amounts of each constituent is dependent principally upon the total concentration of the two solutes, and is almost independent of their proportion. (See Table II.) Thus, a solution containing 50 g. per kg. of copper sulfate and 150 of sulfuric acid has practically the same density (1.1355) as has a solution containing 100 g. per kg. of copper sulfate and 100 of sulfuric acid (1.1350). This simple relation, which is apparently only a mathematical coincidence, has been used as the basis for the curve shown in Fig. 2 in which the total concentration, in g. per liter,¹ of copper sulfate plus sulfuric acid is plotted against the density, yielding an almost straight line. The application of such a curve, or of the table derived from it (Table III) in determining the composition of unknown solutions, is obvious, involving only a determination of the density and acidity, the latter then being deduced from the total concentration corresponding to the observed density, to obtain the copper sulfate concentration.

Details of the application of this table in the regulation of electrolytic copper baths will be given in the second edition of Bureau of Standards *Circular 52*.

In conclusion, the authors desire to acknowledge their indebtedness to Dr. William Blum and Mr. H. W. Bearce under whose direction this investigation was made.

WASHINGTON, November 27, 1915.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN.]

THE RELATION OF OSMOSE OF SOLUTIONS OF ELECTROLYTES TO MEMBRANE POTENTIALS. THEORETICAL.

BY F. E. BARTELL AND C. D. HOCKER.

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The fact that the osmose of solutions of electrolytes shows a close relationship to the differences of potential, which have been found to exist between the two faces of membranes separating such solutions from water, lends support to the theory that the osmose of such solutions is largely dependent upon the electrical condition of the membrane in question. In attempting to explain the osmose of salt solutions by an electrical theory similar to that used to account for electric osmose, two determining factors must be considered: (1) the electric charge of the membrane ma-

¹ Obviously, the above relation exists whether the concentration is expressed in g. per kg. or g. per liter. The data shown in Fig. 2 and Table III have been calculated to g. per liter since the results of the analysis of solutions are usually expressed in that form.

terial with respect to the liquid layer along the capillary tubes of the membrane (*i. e.*, the value of the electrical double layer existing between the membrane and solution), and (2) the polarization of the membrane (*i. e.*, the difference of potential existing between the two faces of the membrane).

Cohen¹ was led to the conclusion that a substance having a lower dielectric constant than the liquid in which it is placed assumes a negative charge. Porcelain, then, placed in water would bear a negative charge and the outer layer of water the corresponding positive charge. The value of this charge is materially altered by traces of acids or alkalis. Perrin² concluded that a concentration of 0.000001 *M* acid or alkali is great enough to determine the sign of the charge of such a membrane as porous chromium chloride. He suggested that a close analogy exists between the effect of ions on the charge of the membrane and the precipitative power of ions for colloids. Both are generally believed to be due to an alteration of the charge of the solid phase by adsorption of the charged ions.

Undoubtedly, then, the sign of the charge on the membrane is influenced by the relative adsorption of the cation and anion from the solution of the electrolyte with which the membrane comes in contact. Bancroft³ has been led to the conclusion that adsorption is a specific process, the neutralization of the charge on a given colloid depending on the nature of the colloid, and upon the nature of both cation and anion. These considerations throw some doubt on the generally recognized belief that hydrogen and hydroxide ions are always adsorbed more than other ions, and hardly justifies the view held by Perrin⁴ and Girard⁵ that the sign of the charge of a body in media of various electrolytes is always attributable to a small preponderance of H or OH ions.

Although the porcelain membranes used in this work probably cannot be termed true colloidal substances, a close analogy is not essential to the conception of their contact electrification in water or solutions. The fundamental ideas used here to explain the unusual osmotic effects observed has as its basis the contact electrification of the porcelain. That the porcelain used in the osmotic experiments actually carries a negative charge has been shown conclusively by the unpublished researches carried out in this laboratory. In neutral solution, under stress of potential, particles of the porcelain finely ground have been found to move toward the anode as though charged negatively. When suspended in very dilute nitric acid they still migrate as though charged negatively, but with a

¹ *Wied. Ann.*, 64, 217 (1898).

² *J. chim. phys.*, 2, 601 (1904).

³ *J. Phys. Chem.*, 19, 394 (1915).

⁴ *Compt. rend.*, 136, 1447 (1903).

⁵ *Ibid.*, 146, 927 (1908).

smaller velocity. The velocity at which they migrate becomes smaller and smaller as the concentration of the acid is increased, until at a concentration of about (0.002 *M* they reach a turning point, after which they move in the opposite direction. It is interesting to note, however, that the velocity after the reversal does not increase nearly so rapidly with the increase in the concentration of the acid as the velocity in the opposite direction decreases before the reversal. This is probably due to conduction taking place through the medium of the acid rather than by migration of these particles. The velocity of migration of these particles can hardly be considered as a measure of the charge they carry when the concentration of the electrolyte becomes very great, but this velocity is probably a measure of what the electric osmose would be if the porcelain were in a fixed position as a membrane. Neither can it be stated with certainty that the turning point in the charge of the membrane would be at exactly the same concentration of acid as the turning point of these porcelain particles.

To sum up the above considerations: Porcelain immersed in water bears a negative charge, and the layer of water immediately adjacent, the corresponding positive charge. The sign of the charge of the membrane in solutions of electrolytes is influenced by selective adsorption of the ions. There are many cases which indicate that adsorption is specific and not rigorously a function of the valence of the ions; and also that other cations may be as strongly adsorbed as the hydrion. In the light of these facts it does not seem unreasonable to assume that ions other than H and OH may be considered effective in determining the sign of the membrane; and further, that cations for which the porcelain shows a strong preferential adsorption may decrease the magnitude of the negative charge assumed by the membrane when immersed in water, or may even reverse the electrical sign of the membrane.

If adsorption is considered as instrumental in determining the charge that the membrane assumes with respect to the movable water layer, then the possible effect of adsorption on the orientation of the membrane must also be considered. If there is a strong tendency for a selective adsorption of one of the ions, the end of the membrane in contact with the solution of the electrolyte would have more opportunity to become charged with electricity of the kind carried by that ion than the face of the membrane in contact with water or a much more dilute solution. In the case of a salt for which there is a selective adsorption of the cation the membrane potential would be increased above that of the contact potential provided the anion is more rapidly moving, and decreased if the cation is the more rapidly moving. Conversely, for a salt in which the anion is the more strongly adsorbed, the membrane potential would be greater than Nernst's formula demands provided the cation is the more

rapidly moving, and less if the anion has the greater velocity. This speculation leaves unsettled the question whether it is possible to think of the migration velocities of the ions as being independent of the amount of adsorption which the ions undergo, or of being independent of the concomitant charge of the water layer along the capillary spaces of the membrane.

The Assumptions Used in this Paper to Explain the Osmotic Effects Observed.—In the light of the above theoretical considerations, experimental evidences seem to point to certain assumptions as the most reasonable to explain the osmotic effects observed. The assumptions used as a working basis in this paper are summed up in the following:

(1) The abnormal osmose is due primarily to an electrical effect and is analogous to electric osmose.

(2) This osmose is brought about by the passage of a charged liquid layer along the capillary tubes of the membrane. The passage of this liquid layer is caused by the driving force of a difference of potential which acts as though it were set up between the two faces of the membrane.

(3) The charge on the membrane—and hence, the charge on the liquid layer—may be modified or the sign may even be reversed by selective adsorption of the ions of electrolytes; and other ions than H and OH may materially affect the charge on the membrane.

(4) The difference of potential, which seems to act between the two faces of the membrane is primarily due to contact electrification, the magnitude of which is dependent upon a difference of migration velocities of the ions in the membrane. However, this difference of potential may be altered by other factors such as adsorption.

(5) The osmose is related to diffusion, for it seems that diffusion of the ions determines to a large extent the polarization of the membrane.

(6) The extent of osmose may be affected by the relative volumes of water and salt solution on the two faces of the membrane, inasmuch as this factor may affect the diffusion of the salt through the membrane.

The membrane when immersed in water or any electrolyte in which there is little tendency for preferential adsorption of ions bears a negative charge and the water layer adjacent bears a corresponding positive charge. Cations are much more adsorbed than anions, the negative ions with the possible exception of OH and a few polyvalent ones having little effect on the charge of the membrane. The alterations of the charge of the walls of the capillary tubes of the membrane by an adsorbed ion will be greater the higher the concentration of the electrolyte. The potential between the two faces of the membrane will be in the direction that Nernst's theory requires, and will be greater the greater the concentration of the electrolyte unless some effect as adsorption interferes.

If the movable water layer and the solution end of the membrane are charged with electricity of opposite sign then the osmose will be positive; if they are charged with the same sign the osmose will tend to be negative.

Applications of the Assumptions to the Experimental Facts.—By application of the assumptions outlined above, it is possible to ascribe an explanation to most of the osmotic effects observed and described in the preceding paper.

Consider first the osmose of nitrates of different concentrations. Potassium nitrate shows positive osmose increasing continuously as the concentration increases up to $0.05\ M$, after which the osmose decreases. The electrical orientation of the cell is the same at all concentrations, and the difference of potential of the two ends of the membrane is appreciable despite the fact that there is little difference of migration velocities of the ions when the membrane is not considered. Above the concentration of $0.05\ M$ the negative charge of the membrane will become materially lessened owing to the selective adsorption of the potassium ion. The positive osmose then decreases as the concentration increases, becoming practically zero or slightly negative at the concentration of M . In double cells, in which the volume of water is small on the water side of the membrane, the rate of diffusion of potassium nitrate soon decreases owing to an equalizing of the concentrations of the salt on the two sides of the membrane. Because of this effect on the rate of diffusion, the membrane potential in the double cells is neither as great, nor able to be maintained as long as in single cells. Hence the positive osmose is less and reaches its maximum much more quickly.

Ammonium nitrate acts in all ways analogous to potassium nitrate. It has been shown that sodium and lithium possess little tendency for adsorption with this porcelain,¹ and the osmotic effect of the nitrate decreases as the concentration increases. Negative osmose of greater numerical value is shown by lithium which has the greater difference in migration velocities, and hence the greater cell potential.

The bivalent cations, Zn, Mn, Mg, and Ba, show decreasingly positive effects as the concentration increases; however, the negative effects do not increase nearly so rapidly as the concentration increases. With manganese, for which tests were made at concentrations as high as M , the negative effects began to decrease numerically at these higher concentrations. This may be explained by assuming either that the natural tendency to give positive effects, such as sugar displays at these concentrations, causes the numerical decrease in negative osmose; or that at these higher concentrations the manganese ion is adsorbed enough to materially lessen the negative charge of the membrane. The latter explana-

¹ From unpublished data obtained in this laboratory.

tion can hardly be disregarded when attention is called to the fact that the higher concentrations of sodium and lithium, isotonic with those of manganese, do not tend to give decreasingly numerical negative effects as the concentration increases.

Aluminium and thorium nitrates give positive effects at all concentrations, a fact which indicates that with these solutions the face of the membrane in contact with the solution bears at all times the sign opposite to that of the movable water layer. The measurements of the cell potential for aluminium show that the orientation is the same as that required by the migration velocities, but somewhat larger than migration velocities would require. Hence, the movable water layer must be negative, a condition which is brought about by the adsorption of the polyvalent cation by the membrane, or by the presence of acid in these salt solutions which cannot be prepared neutral.

The osmose of salt solutions which were made to contain small amounts of acids or alkalis in addition to the salt show that the sense of the osmose is not easily determined by the presence of small amounts of acids or alkalis.¹ It has been pointed out that the effect of small amounts of acid or alkali are not additive in producing the resultant osmose. In one case the addition of a certain amount of acid or alkali to a salt may make its osmose more positive, whereas the addition of the same amount of acid or alkali to another salt may make the osmose of that salt less positive. Thus 0.001 *M* nitric acid decreases the positive osmose of 0.1 *M* potassium nitrate and at the same time numerically decrease the negative osmose of 0.1 *M* lithium nitrate. It seems more logical, then, to assume that the alteration of the osmose by the addition of acids or alkalis depends on the alteration of the electric charge on the walls of the capillary tubes of the membrane, rather than upon any additive polarizing effect that would be produced by diffusion of the acid or alkali through the membrane. With potassium nitrate, the presence of OH ions when alkali is added does not decrease the negative charge on the membrane and experiment shows that the positive osmose is not lessened. When acid is added the presence of H ions does decrease the magnitude of the negative charge of the membrane and the osmose is materially decreased. Similarly, for lithium nitrate the presence of acid decreases the negative charge of the membrane, thereby lessening the passage of liquid through the capillary tubes of the membrane, while the presence of alkali does not materially affect this charge. Similar reasoning may be applied to other salts where the effects produced by the addition of small amounts of acid or alkali are conclusive enough to admit of a definite interpretation. With aluminium nitrate the presence of a small amount of acid increases the osmose. This substantiates the supposition that

¹ The results mentioned in this paragraph are taken from unpublished data.

the membrane is charged positively with this salt and the presence of a small additional amount of acid increases the magnitude of this positive charge.

The effects given by the nitrates of potassium, lithium and barium when the osmose is tested by completely immersing the membranes in acids and alkalies are amenable to similar interpretations. Potassium nitrate gives greater positive effects when the membrane is immersed in alkali than when immersed in acid. The osmose in acid becomes very small or even slightly negative when enough acid is added to reverse the sign of the membrane. Lithium and barium nitrates also show relatively little osmose when the membranes are immersed in larger amounts of acid. When the membranes are immersed in alkalies, lithium nitrate shows greater negative osmose and potassium nitrate shows greater positive osmose than in neutral solution. Barium nitrate offers an exception. With this salt the osmose is lessened numerically, and to about the same extent, by immersing the membrane in either acid or alkali. In the presence of large amounts of either acid or alkali, as $0.01\text{ }M$, the osmose of all of these salts is numerically less than that shown by the salt in neutral solution.

In the osmose of hydrochloric acid alone, the membrane must be assumed to have a positive charge at all concentrations of acid great enough to reverse the sign of the membrane. At concentrations below which the osmose displays a minimum, measurements show that the polarization is in the direction required by Nernst's theory. The movable water layer must then be charged positively and the fact that increase in concentration of acid decreases the osmose may be taken as indication that the greater amounts of acid are decreasing the magnitude of the negative charge of the membrane. At higher concentrations the membrane polarization is found to be the reverse of that required by the migration velocities of the ions, but at these higher concentrations the movable liquid layer must be negative. At these higher concentrations, the solution end of the membrane is charged positively and the movable liquid layer bears the opposite sign, so the positive osmose is accounted for. The reverse orientation of the membrane is probably due to the adsorption of H ions charging the solution face of the membrane positively, this factor becoming greater as the concentration increases, and overcoming the tendency for polarization in the usual direction. This assumption is borne out by the knowledge that H ions are readily adsorbed by the porcelain, and by the observation that when the volume of water on the water side of the membrane is increased, that is, when a condition is brought about that facilitates diffusion of the acid, the positive osmose does materially decrease.

In the osmose of sodium hydroxide alone, it must be assumed that

the membrane is negative at all concentrations while the movable liquid layer carries a corresponding positive charge. As the concentrations of this electrolyte are successively increased, the osmose passes through a maximum. Measurements have shown that opposite electrical orientations of the cell exist on the two sides of this maximum. For some reason the cell shows the reverse orientation from that required by difference in migration velocities when low concentrations of the alkali are tested, while at higher concentrations as $0.2 M$ the orientation is in the usual direction. At concentrations of the alkali lower than $0.01 M$, at which the osmose reaches its maximum, the solution side of the membrane is negative, which accounts for the movement of the positively charged liquid layer into the cell. As the concentration of the alkali is increased above $0.01 M$, the solution side of the cell becomes less negative until at the higher concentrations, the orientation of the cell becomes reversed. When this condition is reached the positively charged movable liquid layer passes toward the water side of the cell, giving rise to negative osmose.

A series of experiments similar to those above described for porcelain have recently been carried out with animal and vegetable membranes such as gold beaters skin, and parchment paper. The data obtained are, in many respects, similar to those obtained with porcelain. The results may, for most part at least, be explained by making use of the theoretical considerations outlined above. This data will be published in the near future.

ANN ARBOR, MICH.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN.]

THE OSMOSE OF SOME SOLUTIONS OF ELECTROLYTES WITH PORCELAIN MEMBRANES, AND THE RELATION OF OSMOSE TO MEMBRANE POTENTIAL.¹

BY F. E. BARTELL AND C. D. HOCKER.

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It has been shown in a previous paper in *THIS JOURNAL*² that some salt solutions with certain grades of porcelain membranes give negative osmose, *i. e.*, the direction of flow of the liquid, as a whole through the membrane, is not in the direction usual in the process of osmosis, but is, on the contrary, from the concentrated to the more dilute solution.

It seems reasonable to suppose that in all osmotic experiments there

¹ The work described in this article constitutes part of a dissertation submitted by Carl D. Hocker in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

² *THIS JOURNAL*, 35, 646 (1914).

is a tendency to produce positive osmose, but in some cases the force tending to produce counter or negative osmose becomes the greater. With membranes as nearly semipermeable as copper ferrocyanide the tendency to give positive effects may be very much greater than the tendency to give negative effects. However, the force tending to produce counter osmose may be of considerable magnitude, with the result that the measured maximum pressures resulting from the tendency to produce positive osmose may be less than the theoretical values. This, then, may explain the abnormal osmotic pressure values obtained with the salt solutions investigated by the Earl of Berkeley and Hartley,¹ Morse,² Fouard,³ and others.

The diverse osmotic effects shown by solutions of electrolytes with plant and animal tissues, which have been attributed to an alteration of the permeability of the cell walls, may likewise be explained by making use of the same considerations that are used in the explanation of negative osmose.

The main object of the present investigation has been to study the relation of osmose to membrane potential, and to determine in what manner the osmose varies with the concentration of solutions of electrolyte and with the diffusion of such electrolytes out of the cell. Data are also given which show the effect of the presence of acids and bases on the osmose of some salt solutions.

Experimental.

Apparatus.—The osmotic experiments described in this paper were carried out with simple, single compartment cells such as have been described in a previous article.⁴

The porcelain membranes used in all the experiments were made from a fine-grained, unglazed, porcelain plate obtained from a local dealer. The pore diameters of the largest pores of this porcelain⁵ were about 0.2 micron.

The Osmose of Nitrate Solutions of Different Concentrations.—The osmotic cells, which were of about 6 cc. capacity, were filled with the solutions to be tested and placed in 800 cc. beakers which contained about 750 cc. of water. At the beginning of each experiment the level of the liquid in the outlet tube of the osmometer was adjusted so that it stood about 50 mm. above the stopper of the cell and at the same time level with the surface of the water in the beaker. The volume of the liquid in the beaker was kept constant throughout the experiments by

¹ *Phil. Trans., (A)* 209, 177, 391 (1908).

² "Osmotic Pressures of Aqueous Solutions" (published by the Carnegie Inst. of Washington), 1914, pp. 211-217.

³ *Bull. soc. chim., [4]* 11, 249, 216 (1912).

⁴ *Loc. cit.*

⁵ Bigelow and Bartell, *THIS JOURNAL*, 31, 1194 (1909).

TABLE I.
Correlation of Maximum and Minimum Effects.

Conc.	KNO ₃	NH ₄ NO ₃	NaNO ₃	LiNO ₃	Ba(NO ₃) ₂	Zn(NO ₃) ₂	Mn(NH ₄) ₂	Mg(NO ₃) ₂	Al(NO ₃) ₃	Th(NO ₃) ₄	Sugar.
0.0005 M.....	40	31	34	34.5	41.5	35	33	37.5	35.5	26	26
0.001 M.....	40	35.5	43	38	46.5	38	37.5	41.5	29	27	36
0.01 M.....	63	49	45.5	30	12.5	7	10	14	70	20.5	35.5
0.02 M.....	71	62	32	17	-1	-13	-7	-5	{ above 175 }	164	40
0.05 M.....	77.5	67.5	37	-2	-19	-37	-32.5	-29.5	291	296	40
0.1 M.....	64.5	61	-3	{ below -65 }	-38.5	-45.5	-42	-45	447	479	..
0.2 M.....	46	35.5	-19	-65	-49	-50	-48	{ below -52 }
0.5 M.....	15	4.5	-56	-31.5
M.....	-2.5	5.5	-67	-7
(U-V) ¹	2.9	2.2	-18.2	-28.4	-6.3	-15.1	-17.7	-15.1	-21.8	-38.3	..

TABLE II.

Time, (hrs.).	Concentration 0.1 M.										Solutions of Potassium Salts in Cells.				
	KNO ₃	KCl	KBr	KI	KCNs.	K ₂ H ₂ O ₄	K ₂ SO ₄	K ₂ CrO ₄	K ₂ Fe(CN) ₆	K ₂ Fe(CN) ₆	K ₂ Fe(CN) ₆	K ₂ Fe(CN) ₆	K ₂ Fe(CN) ₆	K ₂ Fe(CN) ₆	K ₂ Fe(CN) ₆
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
24	24	10	9	5	13	29	37	34	92	41	41	43	43	43	43
48	41	28	26	17	36	54	57	55	151	71	71	78	78	78	78
72	51	45	41	29	58	72.5	78	71	185.5	92	92	104	104	104	104
96	57	57.5	51	37.5	*74	83.5	94	81.5	203	104	104	122	122	122	122
120	61	66.5	60	43.5	84	90	104	86.5	212	108	108	134	134	134	134
168	63	76	68.5	53	95	95	113	93	211	113	113	145	145	145	145
216	64.5	80	71	56	100.5	97	115	95	206	113	113	149	149	149	149
(U-V)	2.9	-0.7	-2.9	-1.7	-8.0	32.6	-3.7

¹ U values as given by A. Heydweiller, *Z. physik. Chem.*, 80, 281-286 (1915).

careful addition of water from time to time. Maximum or minimum effects were usually obtained within 6 days. The maximum or minimum values, represented in millimeters rise or fall, obtained with nitrate solutions of different concentrations are given in Table I.¹

The data obtained from the foregoing experiments show the following facts:

Of the nitrate solutions investigated some give positive osmose, attaining a maximum as the experiment proceeds; others give negative osmose, reaching a minimum. At concentrations from $0.0005 M$ to $0.01 M$ all of the solutions tried give positive effects.

The positive effects of potassium and ammonium nitrates increase as the concentration increases from $0.0005 M$ to $0.05 M$, and then decrease continuously as the concentration increases; sodium nitrate shows a similar maximum at $0.01 M$, after which the positive effect decreases continuously as the concentration increases; the nitrates of lithium, barium, zinc, manganese, and magnesium give slightly lesser positive effects at $0.0005 M$ than at $0.001 M$, but attain their maximum at this latter concentration, after which their osmose also decreases.

The positive effects of aluminium and thorium nitrates, and sugar increase as the concentration increases.

At a certain concentration, somewhat different for each salt, all of the nitrates investigated except those of aluminium and thorium, give an effect practically zero. This concentration for potassium and ammonium is about M ; for sodium, $0.1 M$; for lithium, $0.05 M$; for barium, $0.02 M$; and for zinc, manganese, and magnesium the values of the concentrations lie between $0.02 M$ and $0.01 M$.

In no case is the decrease in positive effect directly proportional to the increase in concentration. The tendency to give counter effects increases more slowly than the concentration.

The trivalent and quadrivalent cations (aluminium and thorium) give unmistakably greater positive effects than the cations of lower valence after the concentration has been increased to $0.02 M$, but their effects at lower concentrations are not greater than those of other salts. The salts of all the divalent cations investigated give lesser positive effects than aluminium or thorium above this concentration of $0.02 M$, but their tendency to give positive effects does not, in turn, exceed those of the univalent cations at this concentration. In the cases of sodium and lithium the counter effects do come to exceed numerically the counter effect of the divalent metals at the concentration of $0.5 M$ or greater, but the osmose of potassium and ammonium nitrates does not become appreciably less than zero at a concentration as great as M . It seems,

¹ For purposes of later comparison the values of differences in migration velocities between the cations and anions of these salts ($U - V$) are appended to the table.

then, that there is no well-defined regularity between the valence of the cations in these salts and the osmotic effects the salts produce.

However, there is some regularity between the difference in migration velocities and osmotic effects. When the value $U - V$ is negative, negative osmose is obtained at some concentration except in the cases of aluminium and thorium nitrates; and, in general, the greater this numerical negative value, the greater the counter osmose. The decreasing positive effect of potassium and ammonium nitrates at concentrations greater than $0.05 M$ is not in accordance with the fact that the $U - V$ value for these nitrates is positive.

The Osmose of Some Salt Solutions of the Same Cation (Potassium Salts).—Experiments were carried out to investigate the osmose of salt solutions with a common cation. For these tests potassium salts were employed, and the concentration chosen was $0.1 M$. These experiments were made with cells submerged in a beaker of water as above described. The results, together with the difference in migration velocities for the ions of some of these salts, are given in Table II.

From the above results it may be pointed out that:

At the concentration of $0.1 M$ all of the potassium salts investigated give positive osmose.

Among the salts with univalent anions, the order of decreasing positive effects is



In general, the salts of the anions of higher valence appear to give greater positive effects than the salts of the anions of lower valence though there are exceptions. Thus it was found that potassium phosphate gives greater effects than either the ferro- or ferricyanide, and potassium chromate gives lesser effects than the thiocyanate or acetate.

There seems to be no relation between the difference in migration velocities and the magnitude of the osmose.

The Osmose of Acids and Alkalies Alone.—For these tests hydrochloric acid and sodium hydroxide were employed. Carbon dioxide-free water was used to make the solutions of alkali, and the cells were enclosed in bottles of approximately the same diameter as the 800 cc. beakers in which the other experiments had been run. In each case the cell was suspended by its outlet tube from the stopper closing the bottle so that the bottom of the cell was raised about 2 cm. from the bottom of the bottle, which contained about 750 cc. of carbon dioxide-free water; that is, about the same volume as that employed in the tests made in open beakers. A hole in the stopper permitted the access of air to the bottle, and both this opening and the outlet tube of the cell were closed by soda-lime tubes to prevent the absorption of carbon dioxide from the atmosphere. The

experiments with hydrochloric acid were run in open beakers with the same set up as that above described.

Concentrations of both acid and alkali varying from 0.001 *M* to 0.2 *M* were tried, and the results of these experiments are shown in the following tables:

TABLE III.

Osmose of Hydrochloric Acid Alone.¹

Time. (hrs.).	0.001 <i>M</i> .	0.002 <i>M</i> .	0.005 <i>M</i> .	0.01 <i>M</i> .	0.02 <i>M</i> .	0.05 <i>M</i> .	0.1 <i>M</i> .	0.2 <i>M</i> .
0	0	0	0	0	0	0	0	0
12	5	8	5	3	2	6	2	1.5
24	10	13	8.5	5	2	17.5	2	30
48	16	20	14	6	3	38	2	57
72	16	23	21	7	5	57	31	88.5
96	22	24.5	22	10	5.5	66	52	110
120	23	25.5	24	12	6.5	69.5	64	118
144	24.5	27	24.5	14.5	7	72	81	...
168	25	27	25	15	7	73	83	119
192	25	27	25	15.5	7	73	83	119

From Table III it is noted that:

The osmose of the acid is positive at all concentrations. The osmose is about the same at 0.001 *M* as at 0.005 *M*, but falls as the concentration increases above these values, reaches a minimum at about 0.02 *M*, after which the maximum values of the osmose grow greater as the concentration of the acid increases.

TABLE IV.

The Osmose of Sodium Hydroxide Alone.²

Time. (hrs.).	0.001 <i>M</i> .	0.002 <i>M</i> .	0.005 <i>M</i> .	0.01 <i>M</i> .	0.02 <i>M</i> .	0.05 <i>M</i> .	0.1 <i>M</i> .	0.2 <i>M</i> .
0	0	0	0	0	0	0	0	0
12	4	3	3	1	2	1	—7	—4
24	7	7.5	8	6.5	11	1	—19	—29
48	14	15	19	25	22	—5	—23	..
72	20	21	25.5	51	29	—9.5	—34	..
96	23	25.5	47.5	68	34.5	—14	—40.5	..
120	25	28.5	59	75	39	—14.5	—45	..
144	26	30.5	65	81	41.5	—15	—45	..
168	27	32	68	83	44.5	—10
192	27.5	32.5	67	84	48

From Table IV it is noted that:

The osmose of sodium hydroxide is positive at concentrations of 0.02 *M* or less, and negative at higher concentrations. The osmose increases from 0.001 *M* to 0.01 *M* as the concentration increases, after which the osmotic effect decreases with increase in concentration, becoming negative at 0.05 *M* and increasingly negative at greater concentrations.

¹ Difference in migration velocities ($U - V$) for the ions of $\text{HCl} = 252.6$.

² Difference in migration velocities ($U - V$) for the ions of $\text{NaOH} = 130.4$.

It is a peculiar fact that the turning point for both the acid and the alkali is at about the same order of concentration, namely $0.01\text{ }M$ to $0.02\text{ }M$.

The difference in migration velocities of the ions for both the acid and the alkali being a constant factor at all times, Nernst's theory of potentials would require that the potential due to the contact of two concentrations of a solution should be a logarithmic function of the ratio of their concentrations, and that an increase in this ratio (*i. e.*, an increase in the concentration of the electrolyte in the cell) should increase this potential. This factor of difference in migration velocities in the cases of the acid and alkali is not sufficient to account for the fact that the osmose is not a continuously increasing or decreasing function of the concentration.

The Osmose of Some Salt Solutions with the Membranes Immersed in Acids or Alkalies of Different Concentrations.—From the data obtained in the foregoing experiments, considerable regularity seemed to exist in many cases between the osmotic effects and the difference in migration velocities of the ions of the electrolyte solutions. This observation lent support to the assumption that the results produced might be due to an electrical effect, the factor of relative differences in migration velocities giving rise to different membrane potentials. If, however, the direction of the flow of the liquid is similar to the direction in electric osmose, both the polarization of the membrane and the sign and magnitude of the charge of the liquid layer adjacent to the walls of the capillary tubes of the membrane should influence the magnitude and perhaps even the sense of the osmose. This latter factor would probably be influenced by the presence of acids and bases which, according to the theories of Perrin¹ and Girard,² is the determining factor of the sign of the membrane.

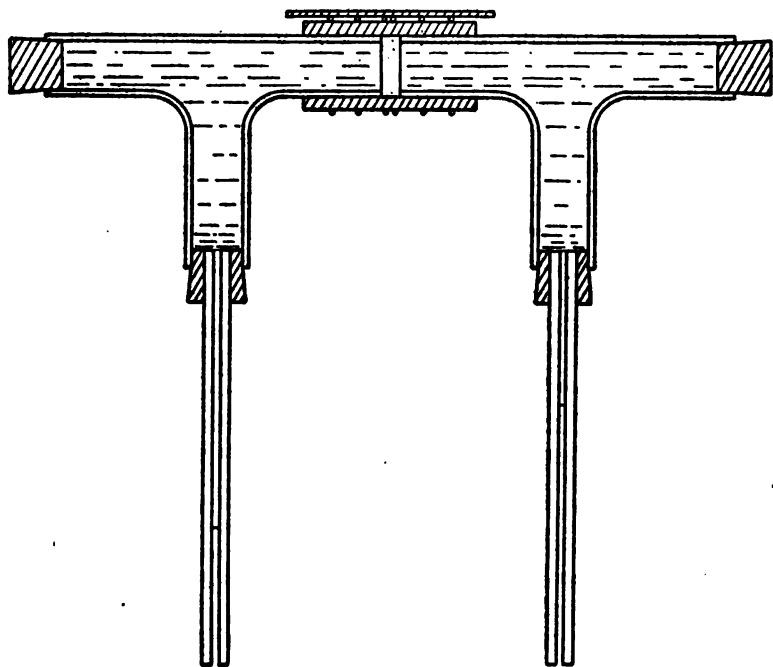
To test this assumption, various attempts were made to determine the osmose of salt solutions with the variation that the membranes of the cells were kept in contact with acids and alkalies. For these tests $0.1\text{ }M$ salt solutions were used, and acid and alkali of concentrations varying from $0.0001\text{ }M$ to $0.01\text{ }M$. The membranes were first washed by drawing water through them for several hours, after which the acid or alkali of the concentration to be used was drawn through until the membrane in each case was thoroughly saturated. The experiments were then carried out with both faces of the membrane in contact with this acid or alkali while the salt solution to be studied was in contact with one face of the membrane. Attempts were first made to study the effect of the presence of acid and alkalies on the osmose of the salt solutions by employing the same type of cell as had been used in the previous experiments. However, it was found even though great precau-

¹ *Loc. cit.*

² *Compt. rend.*, 146, 927 (1908); 150, 1446 (1910); 153, 401 (1911); 159, 99 (1914).

tions were taken to previously saturate the membrane with the acid or alkali solution, that when a cell was filled with this solution and immersed in a bath of the same acid or alkali, there resulted an appreciable osmotic flow.

It was thought that a trace of dissolved membrane material might cause the solution within the cell to become more concentrated in respect to dissolved material, and that this might be the cause of the failure to give alkali blanks. It was found that this effect shown by the acid and alkali blanks could be obviated by the use of cells in which the volumes of solutions on the two sides of the membrane were the same. The type of cell used for this purpose is shown in Fig. 1.



The two compartments are glass T-tubes, each having a capacity of about 20 cc. The porcelain membrane, as in the other cells, is held in place by tightly wound copper wires, and to support the cell upright legs of heavy copper wire are used. Throughout the experiments the cells were kept in a constant temperature bath maintained at 20°. Considerable difficulty was encountered in making the stoppers water tight. In spite of precautions the fall in one outlet tube would, in some cases, be a few millimeters greater than the rise in the other. Because of this source of error, the data obtained with these cells cannot be regarded as quantitative, but this error is never great enough to change the sense, or

even the magnitude, of the osmose by more than a few millimeters. Some of the advantages of this type of cell are as follows: (1) Any leak in the apparatus is readily detected. (2) A change in temperature causes approximately the same rise in both the capillary outlet tubes (*i. e.*, the hydrostatic pressure on the membrane is practically unaltered by any temperature change). (3) In case any membrane material is dissolved the change in concentration will be the same in the two compartments. (4) The openings of the apparatus to the atmosphere are easily protected from entrance of carbon dioxide, etc.—an important factor when alkaline solutions are used. (5) Evaporation of solutions is practically eliminated.

To determine the effect of the presence of acids and bases on the osmose, experiments were made with 0.1 *M* solutions of three typical salts: potassium, lithium and barium nitrates. Table V shows the effect of these salts with this type of cell in neutral solutions, in hydrochloric acid, and in sodium hydroxide of different concentrations. A positive effect signifies a flow of solution toward the side of the membrane in contact with the salt solution, and a negative effect signifies a passage of solution in the opposite direction. Maximum and minimum values were usually obtained after five or six days. The osmose is expressed in millimeters and the values given are half the difference in height of the water levels in the two outlet tubes. The actual hydrostatic pressure is twice this value.

TABLE V.
Comparison of Maximum and Minimum Values.

Salt.	Concentration of NaOH.			Neutral.	Concentration of HCl.		
	0.01 <i>M.</i>	0.001 <i>M.</i>	0.0001 <i>M.</i>		0.0001 <i>M.</i>	0.001 <i>M.</i>	0.01 <i>M.</i>
KNO ₃	9	30	17.5	9.5	5.5	—1	—3
LiNO ₃	—26.5	—32	—35	—26.5	—33	—8	—1
Ba(NO ₃) ₂	—6	—13	—18	—25	—25	—9	—9

From these experiments with the membranes immersed in acids and alkalis it may be pointed out that:

The presence of acids or alkalis is not sufficient to definitely determine the direction of the osmose, but their presence may alter the osmose so that the results are different from those obtained in neutral solution. In general, the presence of acid has a more marked effect on osmose than the presence of alkali.

0.1 *M* potassium nitrate shows less positive osmose in the presence of 0.01 *M* sodium hydroxide than when 0.001 *M* sodium hydroxide is used, but as the amount of alkali is decreased below 0.001 *M* the osmose decreases, shows a lesser value at the neutral point, and decreases continuously as greater amounts of acid are added until with the stronger acid solutions the osmose appears to be slightly negative.

The osmose of lithium nitrate becomes less negative as the concentra-

tion of either acid or alkali is increased above $0.0001 M$. In neutral solution it is, however, less negative than when either acid or alkali of $0.0001 M$ concentration is present.

The minimum effect with barium nitrate seems to be about the neutral point, and the osmose is materially lowered by the presence of amounts of acid or alkali $0.001 M$ or greater.

In all cases, it was noticed that the greatest activity of potassium nitrate came within the first 24 hours, while lithium and barium nitrates showed considerable activity after this period.

Experiments, similar to those just described, were made with solutions of aluminium and thorium nitrates and the following facts noted:

In the presence of acid of concentration as great as $0.01 M$ the osmose is much less than when solutions of these salts alone are used in the cells.

The osmose of thorium nitrate is unmistakably greater than that of aluminium nitrate, whereas when no acid is used in the system there is scarcely enough difference in the effects shown by the two salts to state definitely that thorium nitrate gives the greater effect.

Relation of Osmose to Diffusion.—In order to obtain more information on the mechanism of the osmose of electrolytes with these porcelain membranes, and to learn more about the factors that might influence the electrical orientation of the membranes, a study was made of the rate of diffusion of some electrolytes out of the cells during the process of osmosis. The series of potassium salts whose osmose is recorded in Table II were chosen. As the data in this table were being taken, the course of the osmose was watched, and a time noted (at the end of nine days) when practically all of the cells had just attained their maximum. The cells were then removed from the beakers and analyses made of the solutions left in the beakers. Determinations were made of all of the salts except the nitrate and acetate.

TABLE VI.
Diffusion of $0.1 M$ Potassium Salts Out of Cell.

	Salt.	KCl.	KBr.	KI.	KCNS.	K ₂ SO ₄ .
Osmose at end of 9 days.....		80	71	56	100.5	115
Vol. of cell in cc.....		5.8	5.7	5.8	5.75	6.1
No. of mols of salt in cell....		0.00058	0.00057	0.00058	0.000575	0.00061
No. of mols diffused out.....		0.000398	0.000363	0.000297	0.000409	0.00023
Per cent. diffused out.....		68.5	63.7	51.2	71.1	37.7
		K ₂ CrO ₄ .	K ₂ PO ₄ .	K ₃ Fe(CN) ₆ .	K ₄ Fe(CN) ₆ .	
Osmose at end of 9 days.....		95	213	113	149	
Vol. of cell in cc.....		5.7	5.5	5.7	5.15	
No. of mols of salt in cell....		0.00057	0.00055	0.00057	0.000515	
No. of mols diffused out.....		0.000164	0.000128	0.00018	0.000219	
Per cent. diffused out.....		28.6	23.3	31.8	42.5	

To afford a basis for comparison the volume of each cell when it was set up was measured to within 0.05 cc., and from this volume and the strength of the solution, the number of molecular equivalents originally contained in the cell was calculated. In the following table the number of molecular equivalents contained in the cell in the beginning are compared to the number diffusing out, and the relation between the two expressed as percentages of salt diffused out.

From Table VI it may be noted that:

In the case of the salt with univalent anions, the greater the positive osmose the greater the diffusion of the salt out of the cell.

For salts with bivalent anions, potassium sulfate, which gives the greater osmotic effect, shows greater diffusion than potassium chromate.

For the salts with the anions of higher valence, potassium phosphate offers an exception. It gives the greatest osmotic effect but also shows least diffusion. This case may be an exception either because of the high alkalinity of tertiary potassium phosphate, or because the soluble calcium in the membrane may tend to hold back the phosphate diffusing out.

There seems to be no striking regularity between the amount of diffusion shown by these salts and the valence of the anions.

The amount of diffusion observed here does not seem to be in any way related to the product or difference in the migration velocities of the ions in aqueous solution.

Relation of Osmose to Membrane Potential.—In an attempt to determine whether there was any relation between the charge existing on the two faces of the membrane and the osmose produced by that membrane, measurements were made of the actual potential differences existing between the solutions bathing the faces of the membrane. To make the measurements of these potentials, the cells, previously washed with water, were set up exactly as when the osmose was to be determined. They were then allowed to stand various lengths of time and the potentials of the cell systems measured. Calomel electrodes, a potentiometer, and a delicate galvanometer were used for measuring the potentials. One electrode was brought in contact with the solution and the other in contact with the water, giving the chain: $\text{Hg} - \text{HgCl} - N \text{ KCl} - \text{solution} - \text{membrane} - \text{water} - N \text{ HCl} - \text{HgCl} - \text{Hg}$. These measurements are not always reproducible within narrow limits, but the orientation of the cell system with any given concentration of a salt solution was found to be the same in every case when the measurement was repeated. Further, with any series of salts, the order of magnitude of potential differences was found to be reproducible. The data given in the following experiments were obtained by averaging the readings of the potentiometer taken every five or ten minutes successively for thirty

minutes to an hour. In some cases immediately after the difference of potential had been tested in the cell, the solutions were poured into cylinders, connected directly by a siphon without the interposition of a membrane, and measurements made of the potential set up by these systems. In the data subsequently tabulated, such measurements are found under the columns headed: No membrane after standing. In the following data, a + sign signifies that the face of the membrane in contact with the solution is positive, and a — sign means that the solution side is negative:

TABLE VII.

System.	Differences of potential in the cell after standing		No mem- brane after standing 24 hrs.	Maximum osmose given in cells.	
	24 hrs.	36 hrs.		Single.	Double.
0.1 <i>M</i> KNO ₃ H ₂ O....	—0.0060	—0.0060	—0.002	64.5	9.5
0.1 <i>M</i> Li(NO ₃) H ₂ O...	0.0051 (1)	0.0066			
	(2)	0.0072	0.022	—31	—26.5
0.1 <i>M</i> NaNO ₃ H ₂ O...	0.0038	0.0039	0.006	—3	..
0.1 <i>M</i> Ba(NO ₃) ₂ H ₂ O.	0.0158	0.0161	0.018	—38.5	—25
0.1 <i>M</i> Al(NO ₃) ₃ H ₂ O..	0.0310	0.0303	{ slightly above 0.015 }	447	positive
<i>M</i> KNO ₃ H ₂ O..... (1)	—0.0070				
	(2)	—0.0048	—0.0025	—3	slightly positive
<i>M</i> NaNO ₃ H ₂ O..... (1)	0.0048				
	(2)	0.0071	0.0070	—67	negative

From Table VI it appears that:

The orientation of the cell system in every case is as Nernst's theory of potentials requires, that is to say, the side of the dilute solution is always charged with the sign of the more rapidly moving ion. However, the potential differs in some cases from that which exists without the interposition of the membrane. Thus with potassium and aluminium nitrates the potential difference is greater than when no membrane is interposed; while with lithium, sodium, and barium nitrates, the potential difference is less than when no membrane is interposed. In the case of the 0.1 *M* solutions, the greatest relative variation in the potential difference with and without the interposition of the membrane is shown in the case of lithium nitrate.

Except in the case of aluminium nitrate, those nitrates which show the solution side negative to the water side, give positive osmose.

The cell potential produced by the 0.1 *M* solutions of some univalent potassium salts were also measured. The results of a determination of the potential differences shown by these potassium salts are given in Table VIII. For purposes of comparison, values showing the osmose obtained are also given as well as the data showing extent of diffusion of these salts out from the cells.

TABLE VIII.

System.	Cell potential after 24 hrs.	Maximum osmose in single cells.	Diffusion out of cell after 9 da. (p. c.).
0.1 <i>M</i> KCNS H ₂ O.....	—0.0185	100.5	71.1
0.1 <i>M</i> KCl H ₂ O.....	—0.0105	80	68.5
0.1 <i>M</i> KBr H ₂ O.....	—0.0094	71	63.7
0.1 <i>M</i> KNO ₃ H ₂ O.....	—0.0060	64.5	..
0.1 KI H ₂ O.....	—0.0055	55	51.2

From Table VIII it is noted that:

The order of potential difference is the same as that of the osmose, the greatest numerical cell potential being associated with the salt solution that gave the greatest osmose.

The order of magnitude of the diffusion of the salt outward from the cell is the same as the order of cell potential; again the salt which shows the greatest cell potential showing the greatest diffusion of the salt out of the cell.

TABLE IX.

The Cell Potential of HCl and NaOH Alone.

System	Difference of potential in cell after standing			No mem- brane after standing 24 hrs.	Maximum osmose in single cells.
	12 hrs.	24 hrs.	36 hrs.		
0.01 <i>M</i> HCl H ₂ O.....	—0.0112	(1)—0.0116 (2)—0.0070		—0.0070	16
0.2 <i>M</i> HCl H ₂ O.....	0.0130	(1) 0.0292 (2) 0.0220	(1)0.0182 (2)0.0125	—0.0350	119
0.01 <i>M</i> NaOH H ₂ O...	—0.0225	—0.0052		0.0075	85.5 strongly negative
0.2 <i>M</i> NaOH H ₂ O....	0.0165	0.172		0.021	

Hydrochloric acid at the concentration of 0.01 *M* shows the solution side of the membrane charged negatively as Nernst's theory of potentials requires. However, at a concentration of 0.2 *M* the solution side is charged positively, although, when the solutions after standing 24 hours in the cell, are poured into cylinders and connected by a siphon without the interposition of a membrane, the potential is in the direction that the consideration of difference in migration velocities demands.

Sodium hydroxide at the concentration of 0.01 *M* in the cell shows the water side of the membrane to be charged positively, and not with the sign of the more rapidly moving ion as is shown by the measurements of the contact potential of the solutions contained in the two compartments, when after standing 24 hours, they are transferred to cylinders and measured. When the greater concentration of the alkali is used, however, the system shows the orientation that would be expected of a concentration cell.

The two concentrations of acid measured here are chosen on opposite sides of the minimum osmose point given by the acid in successive changes of concentration; similarly the two concentrations of the alkali are on op-

posite sides of the maximum given by the base. It is significant that both the turning point in the osmose and the turning point in the orientation of the membrane lie between these concentrations in both the case of the acid and of the alkali.

Some potential measurements were also made with cells containing salt solutions in which the membranes were immersed in acids and alkalis. The results obtained did not show definitely that there is any difference in the cell potential after standing 24 hours whether the membrane is immersed in acid, in alkali, or in neutral solution. Inasmuch as the data thus far obtained do not seem to be conclusive, they are not given in this paper.

Summary.

1. Cells were constructed using porcelain membranes of different degrees of porosity, and measurements were made of the relative pore diameters of these membranes. The grade of porcelain chosen as suitable for the osmotic experiments was such that the diameters of the largest pores were about 0.2 micron.

2. The osmose of solutions of various electrolytes was tested in these cells. The range of substances investigated included: (a) nitrates of several univalent, bivalent and polyvalent cations of concentrations from 0.0005 *M* to *M*; (b) 0.1 *M* solutions of a number of potassium salts; (c) hydrochloric acid and sodium hydroxide at several concentrations from 0.001 *M* to 0.2 *M*; 0.1 *M* solutions of some typical nitrates when the membranes were immersed in different concentrations of acid and alkali.

3. It was found that the osmose of these electrolytes varies in divers ways with the concentration. Some electrolytes give positive effects which increase continuously as the concentration of the electrolyte increases; others give positive effects at low concentrations and negative effects at higher concentrations, the positive osmose decreasing continuously as the concentration of the electrolyte is increased. For some electrolytes there is a concentration which gives the maximum positive osmose, while concentrations either higher or lower give smaller positive effects; and finally for other electrolytes there is a concentration that gives the greatest negative osmose (or least positive) while all concentrations either higher or lower give effects that tend to be more positive

4. At a certain concentration, somewhat different for each salt, all of the nitrates investigated, except those of aluminium and thorium, give an effect practically zero. This concentration for potassium and ammonium is about *M*; for sodium, 0.1 *M*; for lithium, 0.05 *M*; for barium, 0.02 *M*; and for zinc, manganese, and magnesium the values of the concentration lie between 0.02 *M* and 0.01 *M*.

5. Osmose seems to be closely related to the electrical orientation of

the membrane, and to the magnitude of the difference of potential which exists between the solutions bathing the two faces of the membrane. In most cases the orientation of the membrane is that which would be expected from the difference in migration velocities of the ions without considering the membrane, but in a few cases the orientation is the reverse.

6. In all cases of the monobasic salts studied, the greater the rate of diffusion of salt through the membrane of the cells the greater the positive osmose. This rate of diffusion is always closely related to the magnitude of cell potential.

7. The facts brought out seem to indicate that the osmose of these solutions of electrolytes is primarily due to an electrical effect, and is analogous to electric osmose. The explanation which seems most reasonable is that the osmose is due to the passage of a charged liquid layer along the capillary tubes of the membrane under the driving force of a difference of potential which acts as though it were set up between the two faces of the membrane. The charge of the movable liquid layer is determined by the charge which the porcelain assumes when immersed in water, but this charge may be altered by selective adsorption of ions when the membrane is brought in contact with solutions of electrolytes; and other ions than H and OH may effect the charge on the membrane. The polarization of the membrane is probably determined by the relative rates of diffusion of the ions through the membrane, but may be altered by such factors as ionic adsorption.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WISCONSIN.]

THE QUANTITATIVE DETERMINATION OF SILICA.

By VICTOR LENHER AND EMIL TRUOG.

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The conventional method of attack of silicates in general consists in the sodium carbonate fusion, the treatment of this fusion with hydrochloric acid for the purpose of separating out the silicic acid, and the subsequent evaporation for the purpose of dehydrating this silicic acid and rendering the silica insoluble in water and in dilute hydrochloric acid. This method of separating silica from the bases has received a great deal of study, yet the results obtained are not all that might be desired. There is considerable uncertainty regarding the necessary length of time and temperature of dehydration, the need of repeated evaporation, the solubility of silica in acids and in the wash solutions used, and the presence of ferric oxide, alumina, lime, magnesia, potash and soda in the nonvolatile residue which remains when the weight of the silica

is obtained by its loss when treated with hydrofluoric and sulfuric acids. The present investigation was undertaken for the purpose of studying the various errors in the determination of silica with the view of making the determination more accurate and if possible more expeditious.

Fresenius¹ states that direct heating over the lamp is not advisable as in the most strongly heated parts the silicic acid is liable to unite again with the separated bases to form compounds which are not decomposed, or only imperfectly by hydrochloric acid.

Gilbert² investigated the effect of different temperatures of dehydration, and the presence of considerable calcium and magnesium on the solubility and contamination of the silica. He worked with several furnaces lags and orthoclase feldspar. His conclusion may be summarized as follows: Temperatures of dehydration above that of the water bath do not give much higher results for silica, but may increase the impurities in the silica considerably. These impurities cannot be removed by digestion for one hour with strong acid. Calcium and aluminum have no tendency to form silicates even at temperatures up to 280°. When magnesia is present, the best results are obtained by dehydrating at 120°. Higher temperatures may cause the formation of partially soluble magnesium silicate.

Hillebrand³ furnishes data showing that the silica recovered with alumina and other oxides may again be partially lost, due to its increased solubility after the pyrosulfate fusion. This, he states, is an added argument in favor of recovering all of the silica at the outset, since the expectation of recovering all of what remains is based on an erroneous assumption. Because of this he states that Gilbert's results lose much of their value. If this criticism be accepted, Gilbert's results still show that high temperatures of dehydration increase the impurities in the silica, and that the presence of considerable magnesia tends much more than lime and alumina to still further increase the impurities, besides causing more silica to go into solution.

Bloor,⁴ in the analyses of clays, made special note of the residues left after volatilization of the silica, and found lime and magnesia present in amounts ranging from practically nothing to about two milligrams of each. The dehydration was made on a water bath. The total residues averaged about 1% of the separated silica. When the dehydration temperature was raised to 125° the residues were greater, due largely to an increase of lime and magnesia. As possible reasons for the presence of lime and magnesia in the residues, Bloor gives as the causes of

¹ Fresenius, *Quant. Chem. Anal.*, 1, 510 (1904).

² *Tech. Quart.*, 3, 61 (1890).

³ *THIS JOURNAL*, 24, 362 (1902).

⁴ *Ibid.*, 29, 1603 (1907).

error insufficient washing, incomplete decomposition at the outset, contamination from porcelain, and different deportment of clay and rock powder in the fusion.

Hillebrand¹ states that he has tested the residues carefully for lime and magnesia, and finds none of the former present and from nothing to 0.2-0.3 mg. of the latter.

Gooch,² Reckert and Kuzirian indicate that the main source of trouble in bringing precipitated silica to constant weight is not due to the presence of water, but to impurities which are partially volatile. They also indicate that the impurities may consist in part of sodium chloride, which on heating with the blast lamp, gradually loses chlorine and produces sodium silicate.

Bauer³ states that silica may hold hydrochloric acid so strongly that a blast flame will not drive it off. He does not state whether the silica used was free from bases or salts, and hence the presence of chlorides is not precluded and his contention correspondingly loses weight.

Wunder⁴ and Suleimann present results which show that the solubility of precipitated silica increases with the strength of hydrochloric acid used and also with the temperature of digestion.

Hillebrand⁵ states that hydrochloric acid has a marked solvent action on the silica that is obtained in the usual analysis. He states that the use of dilute hydrochloric acid in place of water for washing gave unfavorable results.

Experimental.

Temperature of Dehydration.—Undoubtedly the more complete the dehydration the more insoluble does the silica become to the subsequent acid treatment. The completeness of dehydration is, however, limited by the temperature at which the silica reacts with the chlorides and the time which is permissible to use. The writers have been unable to find in the literature any report of a systematic investigation regarding this reversion temperature at which the bases, especially magnesia, start to combine with silica to a material degree. For the purpose of determining this, the following experiments were carried out in which only materials of known composition and high state of purity were used in order that the conditions could be controlled properly.

Materials Used.—Practically all of the silica on the market contains various bases as impurities. Therefore, silica of a high degree of purity was prepared as follows: Silicon tetrafluoride was evolved by the action of sulfuric acid on a mixture of powdered quartz and calcium fluoride.

¹ U. S. Geol. Survey, *Bull.* 422, 97 (1910).

² *Am. J. Sci.*, 186, 598 (1913).

³ *Tonind. Ztg.*, 37, 89 (1913).

⁴ *Ann. chim. anal.*, 19, 45 (1914).

⁵ U. S. Geol. Survey, *Bull.* 422, 92 (1910).

From the generating flask the gas was conducted through a rubber funnel into water contained in a paraffined beaker. The gelatinous silica which separated out was filtered off, and after thorough washing was heated in a platinum dish with sulfuric acid until copious fumes of sulfur trioxide came off for ten minutes. This was done to drive out the last traces of hydrofluoric acid from the silica. The silica was then washed with pure water and strongly ignited. A 0.5 g. sample of this silica left no weighable residue when treated with hydrofluoric and sulfuric acids and evaporated; hence was considered pure.

A second preparation was made as follows: Pure silicon tetrachloride was dropped into water. After evaporating to dryness, which converted the gelatinous silica which had separated out to the granular form, the material was powdered and treated with sulfuric acid and thoroughly washed in the same way as the silica obtained by decomposing the fluoride. On evaporating a 0.5 g. sample with hydrofluoric and sulfuric acids, a residue of 0.05 mg. was obtained, which is within the limits of error of working. This silica was, therefore, as pure as that prepared from the tetrafluoride. When the silica from the tetrachloride was not treated with sulfuric acid, it contained more impurities. Iron appeared to be the main impurity, and the conversion to the sulfate made its removal by washing possible.

Silica prepared from the tetrafluoride is very light and voluminous, making it difficult to handle and weigh. That prepared from the tetrachloride is more like ground quartz and hence is readily handled.

The hydrofluoric acid used was prepared by redistilling pure commercial acid in a platinum still. A 50 g. sample left no weighable residue on evaporation and ignition.

The supply of sulfuric acid on hand gave on evaporation and ignition a residue of 0.0002%, and hence was sufficiently pure.

The hydrochloric acid used was prepared both by redistilling pure acid, in which case the first and last portions were discarded, and by the action of sulfuric acid on sodium chloride, using appropriate wash bottles.

The other chemicals employed showed by blank tests or otherwise that they were sufficiently pure for the purposes intended.

Analytical Methods.—In our experiments 0.5 g. samples of silica were always used. To the weighed sample were added the various amounts of calcium, magnesium or ferric oxides and from four to six parts of sodium carbonate. The amount of sodium carbonate used was regulated according to the amount of basic oxide added. The materials were mixed in a platinum crucible and heated by means of a burner until the fusion was quiet. The fused mass was then transferred to a platinum dish and treated with an excess of dilute hydrochloric acid (sp. gr. 1.05). After all but the silica had dissolved, the solution was evaporated to dryness

on the water-bath and the residue further heated for two hours at the temperature indicated in each series of experiments. After dehydration, the mass was treated with 25 cc. of hydrochloric acid (sp. gr. 1.1). The dish was covered and digested on the water bath for 10 to 20 minutes. Any lumps appearing were broken up, and after diluting with water, the solution was filtered. The silica was washed with water till the runnings no longer gave a turbidity with silver nitrate. This gave a filtrate of 200 to 300 cc. The silicate was volatilized in a weighed platinum crucible, after the addition of a few drops of sulfuric acid and about 3 cc. of hydrofluoric acid. The residue was ignited and the crucible and contents weighed.

Two double walled drying ovens, one of copper and one of sheet iron, were first used in the dehydrations. They were heated by two Bunsen burners. On testing these ovens carefully, it was found that under the best conditions the temperature at various points on the same shelf in the oven varied as much as 10° and sometimes even more. The ovens were in good condition and the burners were carefully regulated. With less care and the use of two shelves, thermometers variously placed would show a difference if as much as 20° in different parts of the same oven. The experiments with lime and with magnesia given in Table I were carried out in these ovens. In all of the other experiments, except when a temperature higher than 120° was required, an automatic electric oven

TABLE I.
Nonvolatile Residues Using Various Amounts of Basic Oxides.
Dehydration Temperature 110° .

SiO ₂ , g.	Na ₂ CO ₃ , g.	CaO, g.	N. V. R., g.	SiO ₂ , g.	Na ₂ CO ₃ , g.	MgO, g.	N. V. R., g.
0.5000	2	0.0000	+0.0001	0.5000	2	0.0010	-0.0001
0.5000	2	0.0000	-0.0001	0.5000	2	0.0010
0.5000	2	0.0010	-0.0001	0.5000	2	0.0100
0.5000	2	0.0010	-0.0001	0.5000	2	0.0100
0.5000	2	0.0100	+0.0001	0.5000	2	0.5000	+0.0002
0.5000	2	0.0100	+0.0001	0.5000	2	0.5000	+0.0002
0.5000	2	0.0500	+0.0001	0.5000	2	0.1000	+0.0005
0.5000	2	0.0500	..	0.5000	2	0.1000	+0.0001
0.5000	2	0.1000	+0.0001	0.5000	4	0.2000	+0.0003
0.5000	2	0.1000	+0.0001	0.5000	4	0.2000	+0.0003
0.5000	4	0.2000	+0.0002	0.5000	6	0.5000	+0.0003
0.5000	4	0.2000	..	0.5000	6	0.5000	+0.0001
0.5000	6	0.5000	..	0.5000	2.5	0.0100	+0.0009
0.5000	6	0.5000	-0.0003	0.5000	2.5	0.0100	+0.0005
				0.5000	2.5	0.0500	+0.0001
				0.5000	2.5	0.0500	+0.0003
				0.5000	2.5	0.2000	+0.0005
				0.5000	2.5	0.2000	+0.0019
				0.5000	5.0	0.5000	+0.0011
				0.5000	5.0	0.5000	+0.0009

was used, which made it possible to control the temperature to which the dishes were heated to within one degree.

In Table I are given the results when various amounts of calcium, magnesium and ferric oxides were fused with silica and sodium carbonate and where a dehydration temperature of 110° was used. From these data it is evident that lime does not seriously contaminate the silica at this temperature. With the large amounts of magnesia there are indications of contamination, but this is undoubtedly due to the poor regulation of temperature secured with the gas heated oven, as already explained. The results with magnesia given in Table II entirely confirm this probability. The ferric oxide contaminated the silica in all cases in an irregular way.

TABLE II.
Nonvolatile Residues under Different Temperatures of Dehydration.

Temper- ature.	SiO ₂ g.	Na ₂ CO ₃ g.	CaO, g.	N. V. R., g.	Temper- ature.	SiO ₂ g.	Na ₂ CO ₃ g.	MgO, g.	N. V. R., g.
110°	0.5000	2	0.1000	+0.0001	105°	0.5000	2.5	0.1000	+0.0001
110	0.5000	2	0.1000	+0.0001	110	0.5000	2.5	0.1000	+0.0001
115	0.5000	2	0.1000	..	110	0.5000	2.5	0.1000	+0.0001
115	0.5000	2	0.1000	..	115	0.5000	2.5	0.1000	+0.0002
120	0.5000	2.5	0.1000	+0.0002	115	0.5000	2.5	0.1000	+0.0006
120	0.5000	2.5	0.1000	+0.0002	120	0.5000	2.5	0.1000	+0.0010
150	0.5000	2	0.1000	+0.0003	120	0.5000	2.5	0.1000	+0.0012
150	0.5000	2	0.1000	+0.0004	150	0.5000	2.5	0.1000	+0.0008
175	0.5000	2.5	0.1000	+0.0003	150	0.5000	2.5	0.1000	+0.0018
175	0.5000	2.5	0.1000	+0.0004	175	0.5000	2.5	0.1000	+0.0007
			Ferri-oxide		175	0.5000	2.5	0.1000	+0.0011
110	0.5000	2.5	0.0500	+0.0021	Free flame	0.5000	2.5	0.1000	+0.0008
110	0.5000	2.5	0.0500	+0.0028	Free flame	0.5000	2.5	0.1000	+0.0016
120	0.5000	2.5	0.0500	+0.0004					
120	0.5000	2.5	0.0500	+0.0004					
150	0.5000	2.5	0.0500	+0.0015					
150	0.5000	2.5	0.0500	+0.0013					

Table II shows the results obtained when the amount of basic oxide added was constant (0.1 g.), and the temperature of dehydration varied. From these data it is evident that lime does not seriously contaminate the silica, unless the temperature of dehydration is at least over 115° . With magnesia the point at which the silica becomes contaminated with magnesia is reached at 115° . At 110° there is no appreciable contamination, which shows that the slight contamination of magnesia reported in Table I was probably due to the poor regulation of temperature secured with the gas heated ovens.

Ferric oxide contaminates the silica in an entirely irregular way at all temperatures, which suggests that it may be due to physical causes. Undoubtedly on evaporation and dehydration the ferric chloride by hydrolysis changes partly to oxide and oxychloride, which, because of their

lesser solubility, are not as readily removed from the interior of the dried silica as calcium chloride.

Potash and soda have been repeatedly tested for in many experiments, but in our work have never been detected in the nonvolatile residue. This is in accord with the work of Hillebrand¹ but not with the observations of Kuzirian.²

The general knowledge of the contamination of silica by the bases has been emphasized by those who have studied in detail the silica determination. It has been assumed by some that actual reversion to silicate takes place. It is not possible at the present time to state definitely just how these bases are retained by the silica. Hydrolysis alone will not account for the retention of lime or magnesia, since the products of the hydrolysis of calcium or magnesium chlorides are readily soluble in even dilute hydrochloric acid. The subsequent extraction with dilute acid should, therefore, remove the lime or magnesia, but such is not the case. In the case of contamination of the silica by iron, hydrolysis probably can be assumed to be at least one cause.

Adsorption might be advanced as a possible explanation, but would hardly seem plausible. As a matter of fact, the contamination is a very real thing, and in the analysis of silicates always takes place. In the silica from basic rocks the nonvolatile residue is usually very much higher than from those of acidic character.

It should be emphasized at this point that in the regular procedure of a silicate analysis, if the dehydrated silica and chlorides are treated first with water, insoluble basic chloride of iron is formed which will not completely dissolve in hydrochloric acid of any strength in any reasonable length of time. This is especially true when hot water is used. Sufficient hydrochloric acid, therefore, must be added to prevent this decomposition. On the other hand, large excess of hydrochloric acid must be avoided on account of its solvent action on the silica.

Solubility of Silica in Hydrochloric Acid and in Wash Solutions.—In order to determine what effect the concentration of the hydrochloric acid used in taking up the dehydrated silica has on the amount of silica which passes into solution and is recovered in the subsequent dehydration, the following experiments were carried out:

One-half gram of pure silica was fused with 2.5 g. of sodium carbonate, treated with hydrochloric acid, evaporated, dehydrated at 110° for 2 hours and then taken up with hydrochloric acid of different strengths, as indicated in Table III. After filtering and washing to a volume of about 250 cc. the silica in the filtrate was determined by evaporation, dehydration and filtration in the usual way. The results are given in the first three columns

¹ THIS JOURNAL, 24, 373 (1902).

² *Am. J. Sci.*, 37, 61 (1914).

of Table III. The main bulk of silica filtered off after the first dehydration was further treated with acid in order to determine if more silica would go into solution. The silica was transferred from the filter papers to platinum dishes. One series was treated with hydrochloric acid in exactly the same way as before and the dissolved silica determined. The other series were treated similarly with an equivalent amount of sulfuric acid. The results are given in the last two columns of Table III.

TABLE III.
Solubility of Dehydrated Silica in Acid Treatments Indicated.
Grams of SiO_2 Dissolved.

Method of treating dehydrated silica.	First treatment with HCl.			Second treatment with	
	a.	b.	av.	HCl.	H_2SO_4 . ¹
12.5 cc. con. HCl (sp. gr. 1.2) digested 15 min. Dil. to 25 cc. and digested 15 min. Dil. to 50 cc. and filtered.....	0.00251	0.00251	0.00251	0.00068	0.00103
25 cc. HCl (sp. gr. 1.1) digested 30 min. Dil. to 50 cc. and filtered.....	0.00230	0.00212	0.00221	0.00048	0.00136
50 cc. HCl (sp. gr. 1.05) digested 30 min. and filtered.....	0.00410	0.00402	0.00407	0.00286	0.00279

The data in Table III indicate that digestion with concentrated hydrochloric acid or with a considerable volume of dilute acid are both to be avoided. Hydrochloric acid (sp. gr. 1.1) appears to be about the right concentration for the first moistening of dehydrated silica. The amount used and time of digestion should be the minimum.

A comparison of the data in Table III shows that less silica goes into solution in the second treatment. The results corroborate the work of Hillebrand,² who has shown that hydrochloric acid has a distinct solvent action on the silica. Completeness of dehydration is not the only factor that must be considered in accounting for the silica found in the filtrate after the first dehydration. Dilute sulfuric acid has about the same solvent action as dilute hydrochloric acid, while somewhat stronger sulfuric acid has a more marked action.

Although the amount of silica dissolved in the second treatment as given in Table III is less than that dissolved in the first treatment, yet it cannot be concluded from this that there is a definite amount of silica present after dehydration which is more soluble than the rest. In the first extraction with hydrochloric acid there was a considerable amount of sodium chloride present, which, as following results show, has a considerable solvent action on the silica.

Solubility of Silica in Different Wash Solutions.—In order to determine what kind of a washing solution would have the least solvent action on the silica, the following experiments were made. The silica on the filter

¹ The H_2SO_4 was used in amounts equivalent to the HCl.

² THIS JOURNAL, 24, 368 (1902).

papers from the previous work was thoroughly washed with water and then washed with 300 cc. of the respective wash solutions indicated in Table IV. The filtrates were evaporated and the silica determined in each case. The silica in 300 cc. of original wash solution was also determined in each case:

TABLE IV. Solubility of Silica in Wash Solutions. Results in Grams.			
Washed solution used.	SiO ₂ in 300 cc. of blank.	SiO ₂ in 300 cc. after washing.	SiO ₂ dissolved by wash sol.
Distilled water.....	0.00040	0.00106	0.00066
1% HCl.....	0.00030	0.00138	0.00088
1% NaCl.....	0.00016	0.00243	0.00227
1% NH ₄ Cl.....	0.00094	0.00586	0.00492

The data in Table IV indicate that distilled water has the least solvent action of any of the washing solutions used. Solutions of sodium and ammonium chloride have a distinct solvent action. All things considered, a wash solution of distilled water just acidified with hydrochloric is perhaps the most desirable. The presence of a very small amount of hydrochloric acid has no marked solvent effect on the silica, but does have the advantage of helping to remove occluded bases in the silica and preventing the silica from going into a colloidal condition, in which condition it will pass through the filter paper to a considerable extent. A wash solution, consisting of 1 cc. concentrated hydrochloric acid in 100 cc. water, appears quite desirable, and this was later used with good results.

Solubility of Silica as Influenced by Extent and Nature of Dehydration.—It was thought that perhaps if the period of dehydration at 110° was increased over two hours, the silica would be made more insoluble in the subsequent acid treatment. Dehydration at one-fourth atmospheric pressure was also tried. For this purpose a vacuum desiccator attached to a filter pump was placed in the drying oven. Two samples of material, a silicate rock and a clay loam soil, were fused with sodium carbonate and the fusion was treated with hydrochloric acid. The results are given in Table V.

TABLE V.
Solubility of Silica as Influenced by Nature and Extent of Dehydration.

Nature and extent of dehydration.	Material.	Grams SiO ₂ recovered in successive dehydrations.				
		1st dehydr.	2nd dehydr.	3rd dehydr.	4th dehydr.	Total first two dehydr.
4 hr. at 110°, 1/4 atm.....	Blank	0.0008	0.0002	0.0002	0.0001	0.0010
2 hr. at 110°.....	Soil	0.7878	0.0016	0.0003	0.0004	0.7894
4 hr. at 110°.....	Soil	0.7887	0.0019	0.0002	0.0004	0.7906
2 hr. at 110°, 1/4 atm.....	Soil	0.7873	0.0014	0.0003	0.0003	0.7887
4 hr. at 110°, 1/4 atm.....	Soil	0.7876	0.0016	0.0002	0.0004	0.7892
2 hr. at 110°.....	Silicate	0.6491	0.0014	0.0006	0.0003	0.6505
4 hr. at 110°.....	Silicate	0.6511	0.0015	0.0007	0.0003	0.6526
2 hr. at 110°, 1/4 atm.....	Silicate	0.6506	0.0014	0.0007	0.0002	0.6520
4 hr. at 110°, 1/4 atm.....	Silicate	0.6490	0.0016	0.0005	0.0003	0.6506

The results in Table V indicate that there is no advantage in dehydrating more than two hours, or in carrying out the dehydration under reduced pressure. This indicates that the failure to recover all the silica in one dehydration is not due to insufficient dehydration, but to the great opportunity afforded by the large mass of silica for its direct solution during the acid treatment. From this it may be concluded that the dehydrated mass should be taken up with as little acid as possible, and that this acid should be allowed to act only until the bases are in solution and then filtration proceeded with immediately.

In a further experiment the period of dehydration at 110° was extended to 24 hours. In this case the total amount of silica recovered in all of the dehydrations was less by several milligrams than when a 2-hour period of dehydration was used. This indicates that continued dehydration for a long period, at even 110° , may cause the silica to become contaminated with sufficient magnesia to seriously affect the results. It seems that when magnesia thus contaminates silica it is practically impossible by subsequent evaporations with acid and dehydration to render the silica free from magnesia.

Adopted Procedure for the Determination of Silica.

After a careful study of the results thus far reported, the following procedure was adopted:

A one-half to one gram sample of silicate is intimately mixed with 5 g. of sodium carbonate and fused in a platinum crucible. In the case of a limestone, as suggested by Hillebrand,¹ much less flux is required. The cold fusion is treated with 60 cc. of hydrochloric acid (sp. gr. 1.07). After all carbonates are decomposed and the lumps are broken up, evaporation on steam or water bath is proceeded with until the residue begins to powder or crumble. Further evaporation should be avoided. Breaking up of lumps and crusts greatly expedites the evaporation near the end. The residue is treated with 15 cc. of hydrochloric acid (sp. gr. 1.1) covered and heated on the water bath for 10 minutes. After diluting with 10 cc. of water, filtration is proceeded with immediately, and the silica is washed with a hot solution consisting of 5 cc. of hydrochloric acid (sp. gr. 1.2) to 95 cc. of water. This filtration is preferably performed with suction. The filtrate is evaporated to dryness and until the smell of acid has practically disappeared. The residue is dehydrated at 110° for 2 hours, taken up with 8 cc. of hydrochloric acid (sp. gr. 1.1), covered and heated on the water bath five to ten minutes, diluted to about 50 cc. and filtered immediately. This filtration is performed without suction and the washing is done with cold water containing 1 cc. concentrated hydrochloric

¹ THIS JOURNAL, 25, 1202 (1903).

acid to 99 cc. water.¹ The paper and silica from the second dehydration are placed in a platinum crucible and the paper burned. The paper containing the silica from the first dehydration is then added to the crucible and the silica is ignited to constant weight. Great care should be exercised in burning the paper, as the current of air produced by a rapidly burning filter paper is sufficient to carry finely divided silica out of the crucible. Loss in this way is more serious when the amounts of silica are quite large, in which case a platinum crucible of at least 30 cc. capacity should be used. Ignition for about 30 minutes with a Meker burner is usually sufficient to produce constant weight. If the amount of silica is low, less time may be required. Breaking up of crumbs and lumps with a stiff platinum wire aids greatly in burning the last traces of carbon and reducing to constant weight. The silica is then determined by loss, volatilizing in the usual way with hydrofluoric acid after the addition of a few drops of sulfuric acid. The nonvolatile residue is then fused with four times its weight of sodium carbonate and after acidifying with dilute hydrochloric acid is added to the filtrate from the silica which is examined in the usual way for the bases.

Table VI shows the results of analyses by the method given of two silicates, one of which was a feldspar, and two limestones, one of which was dolomitic. The results of a third dehydration are also given. As indicated in the table, porcelain casseroles were used in one set and platinum dishes in the other.

TABLE VI.
Silica Determinations with Adopted Procedure.

Material.	Evaporation in	Grams SiO ₂ and nonvolatile residue recovered in successive dehydrations.							
		First recovery.		Second recovery.		Total first two.		Third recovery.	
		SiO ₂ .	N. V. R.	SiO ₂ .	N. V. R.	SiO ₂ .	N. V. R.	SiO ₂ .	
Blank.....	Plat.	0.0008	0.0003	0.0002	..	0.0010	..	0.0002	
Silicate 8.....	Plat.	0.4372	0.0008	0.0030	0.0004	0.4402	0.0012	0.0003	
	Porc.	0.4329	0.0003	0.0072	0.0005	0.4401	0.0008	0.0010	
Silicate 20.....	Plat.	0.6935	0.0011	0.0033	0.0001	0.6968	0.0012	0.0003	
	Porc.	0.6804	0.0004	0.0166	0.0003	0.6970	0.0007	0.0012	
Limestone 12.....	Plat.	0.0547	0.0003	0.0020	0.0004	0.0567	0.0007	0.0002	
	Porc.	0.0551	0.0003	0.0017	0.0007	0.0568	0.0010	0.0001	
Dolomitic limestone									
13.....	Plat.	0.1889	0.0004	0.0022	0.0003	0.1911	0.0007	0.0001	
	Porc.	0.1880	0.0015	0.0029	0.0001	0.1909	0.0016	0.0001	

The data in Table VI indicate that the method outlined gives very satisfactory results. The duplicates agreed to within 0.1 or 0.2 mg., which is much better than the previous results in Table V. Two evapora-

¹ Often a little silica sticks so tenaciously to the sides of the dish that washing fails to remove it, and in such cases it is best removed with a little piece of ashless filter paper which is subsequently burned with the main precipitate of silica.

tions conducted as stated are sufficient to recover the silica when the acid treatment is performed as outlined. The silica recovered in a third evaporation, when platinum dishes are used, ranges from 0.1 to 0.3 mg. These amounts are of the same order as those obtained in blank determinations or when a fourth evaporation is made, and are to be regarded as due to contamination from the glass beakers, funnels, wash water and acid used. Hillebrand¹ states that from 2-4 mg. of silica remain in the solution after the second evaporation and filtration. The presence of such large amounts has been entirely prevented by the method outlined. The results when porcelain casseroles are used have been favorable. The results of the third evaporation indicate that in certain cases there may be contamination from the porcelain.

In other methods of procedure the nonvolatile residue frequently ranges from 2 to 6 mg. or even much more in basic rocks. In the method outlined this has been reduced with the materials with which we worked to about 1 mg., on the average, for both recoveries of silica. Prevention of excessive drying in the first evaporation and the use of a hot acidified wash solution has made this possible. This is a very desirable feature, as it greatly reduces the time necessary to ignite the silica to constant weight and hence reduces errors incident to long continued heating of platinum and also those which may arise in the correction for impurities which have been suggested by previous workers.

Summary.

The investigation reported was undertaken for the purpose of making the determination of silica more accurate and expeditious. Certain causes of error were first investigated and later remedies worked out and applied. The errors and corrections may be summarized as follows:

Dehydration above 110° leads to erroneous results. Long-continued baking of a *large mass* of silica at 110° is objectionable, since the result is to greatly increase the nonvolatile residue. When natural silicates are analyzed, as is well known, it is impossible to recover all the silica in one dehydration, no matter how complete the dehydration may be. This is due to the fact that silica has a distinct solubility in hydrochloric acid, the extent of which is dependent on the strength and volume of acid used, and time of contact. The presence of considerable impurities in the silica is objectionable, since it greatly increases the time necessary for ignition to constant weight, and may also cause an error in the correction of silica for impurities.

The difficulties just stated are overcome by the modified procedure outlined, the essential features of which are as follows: The main mass of silica is removed after simple evaporation on the water or steam bath till the material begins to get granular but still contains considerable

¹ U. S. Geol. Survey, *Bull.* 422, 94 (1910).

acid and water. In this way opportunity for the contamination of the silica is greatly lessened as is also the amount of nonvolatile residue, which is further decreased by the use of the wash solution recommended. A dehydration temperature of more than 110° should never be used. After the second dehydration, the solution of appreciable amounts of silica is prevented by limiting the amount and strength of acid used and also the period of its contact.

Our experience as well as our students' experience with this procedure as outlined has given more accurate silica results than any other procedure, and with the purpose of calling to the attention of the analyst some of the pitfalls in the determination of silica and in the subsequent determination of the bases, the following observations are appended, all of which our laboratory experience has induced us to emphasize, though some have been repeatedly pointed out:

1. In the sodium carbonate fusion method with silicates, there is always a nonvolatile residue when the silica is volatilized with hydrofluoric and sulfuric acids.
2. The nonvolatile residue contains the various bases, and should be fused with sodium carbonate and added to the filtrate from the silica when the bases are to be determined.
3. In the dehydration of the silica from the hydrochloric acid treatment of the fusion, the temperature should never be allowed to go above 110° .
4. Dehydrated silica is appreciably soluble in hydrochloric acid of all strengths. With the dilute acid used, this error is almost negligible.
5. Dehydrated silica is slightly soluble in solutions of the alkaline chlorides. As sodium chloride is always present from the sodium carbonate fusion, an inherent error is obviously thus introduced.
6. The dehydrated silica along with the mass of anhydrous chlorides must not be treated first with water, since hydrolysis causes the formation of insoluble basic chlorides of iron and aluminum, which do not dissolve completely in hydrochloric acid.
7. Hydrochloric acid (sp. gr. 1.1) in minimum amount should be used first to wet the dehydrated chlorides and should be followed by water to bring the volume to about 50 cc., after which the silica should be filtered off as quickly as possible.
8. Pure silica comes quickly to constant weight on ignition. Slightly impure silica frequently requires long heating with the blast flame in order to attain constant weight, and is then commonly hygroscopic.
9. Evaporations of the acidulated fusion in porcelain give practically as good results as when platinum is used.
10. Filtration of the main bulk of the silica after one evaporation is desirable, inasmuch as the silica is removed at once from the solutions which act as solvents.

11. Dehydration of the silica under reduced pressure has no advantages over the common evaporation at ordinary atmospheric pressure.

12. Excessive time of dehydration, *viz.*, 4 hours, possesses no advantages.

13. Excessive amounts of sodium carbonate should be avoided, since the sodium chloride subsequently formed exerts a solvent action on the silica. The best proportions are 4-5 parts sodium carbonate to 1 of silicate. Less than 4 parts of sodium carbonate is frequently insufficient to completely decompose many silicates.

14. The nonvolatile residue has been found to be invariably free from sodium. Pure silica, on fusion with sodium carbonate, subsequently gives no nonvolatile residue.

MADISON, WISCONSIN.

NOTE.

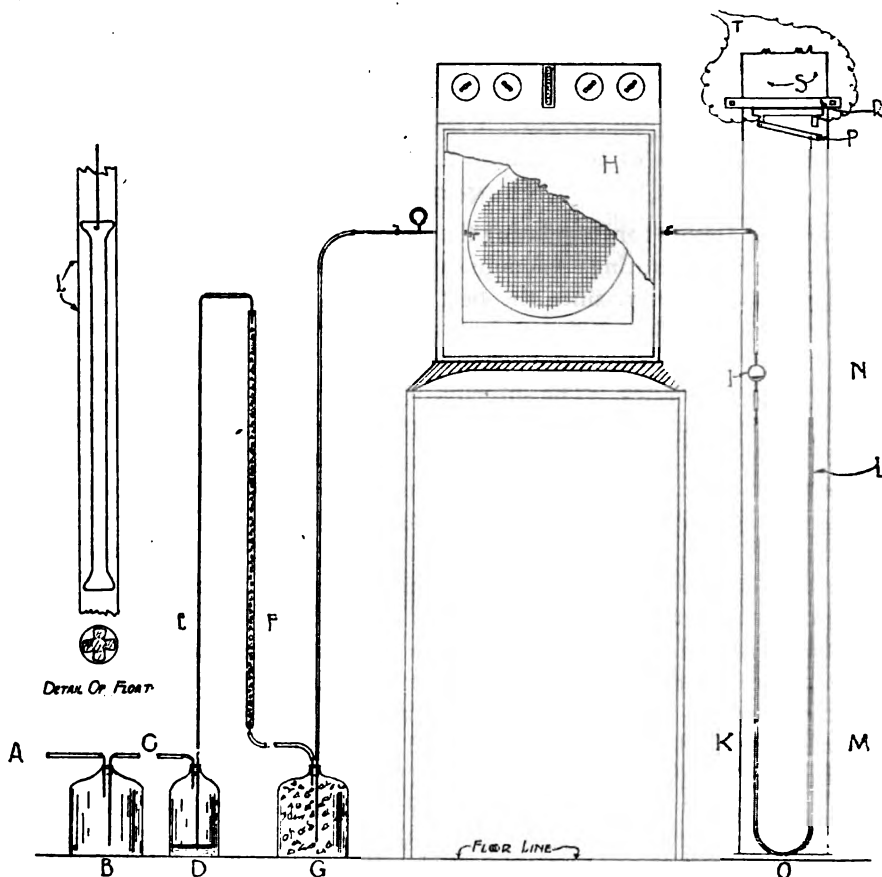
A Simple Device for Regulating the Pump Used in Exhausting a Vacuum Oven.—When operating a vacuum oven it is customary to keep the pump running continuously, since the best ovens on the market will not hold a vacuum more than a few hours, especially at elevated temperatures. With a good pump the initial exhaustion of the oven can be accomplished in a very few minutes. The subsequent leakage of air is, however, so slow that the continuous operation of the pump for days at a time seems a waste of power. The simple device described in this paper can be so adjusted as to start and stop the motor automatically for any desired range of vacuum, thus effecting a considerable saving of power. The materials of which it is constructed are to be found in any chemical laboratory, and very little mechanical skill is required to assemble them.

The oven to which this device was attached is a Freas' Electrically Heated Vacuum Oven connected to a Crowell's Pressure and Vacuum Pump, the latter operated by a one-horse-power motor. When the oven is maintained at 100° temperature and 20 to 60 mm. pressure, the apparatus described below starts the motor 18 to 20 times per hour, allowing it to run about 30 seconds each time. Thus at an average pressure of 40 mm. the pump runs only one-sixth of the time. As stated above, the apparatus may be adjusted for any desired range of pressure, the motor starting at the maximum and stopping at the minimum pressure.

Referring to the diagram, *A* is the tube leading to the vacuum pump. The bottle *B* serves as a trap to catch any mercury that may be drawn out of *D*. The bottle *D* contains mercury, Tube *E* (6 mm. inside diameter) which is about 80 cm. long, projects 1 cm. into the mercury in *D*. When the pump stops, the atmospheric pressure raises the mercury in *E* corresponding to the vacuum, thus closing the chamber. When the pump is running, the air is required to bubble through only 1 cm. of mer-

cury. *F* and *G* are filled with calcium chloride to prevent the water given off by the samples in the oven from contaminating the mercury or the oil in the pump.

To the outlet of the vacuum oven *H* is attached the "U" tube *K L*. This tube, which contains mercury, is supported by the standard *O*. The arm *K* is about 90 cm. long and has an enlargement, *I* (3 cm. in diameter), situated 80 cm. above the lower end. The arm *L* is about 80 cm. long and 12 mm. inside diameter. It contains a glass float, *M*, which is



12 cm. long. This float is in the form of a plunger, with a small bulb at the lower end and small projections near the top. This keeps the float surrounded with mercury and prevents adhesion. The rod *N* connects the plunger *M* with switch *P*, which is an ordinary throw switch on a porcelain back, *R*. This switch is mounted on a block, *S*, which is so made that it can be adjusted by sliding it up and down on the standard *O*. The wires *T* lead to the motor.

When the desired vacuum is reached, block *S* is so adjusted that float *M* will just open switch *P*. As the air leaks into the oven, the column of mercury will raise the float *M* and close the switch, thus starting the pump.

The use of the bulb *I* reduces the pressure required to throw the switch to 25 mm. of mercury in place of 80 mm., the height which would be required were the tube without the bulb.

The above apparatus has been in constant use in our laboratory for two months and has given entire satisfaction.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE CONSTITUTION OF THE THREE SYMMETRICAL DINITROPYROCROLLS.

BY WILLIAM J. HALE AND WILLIAM V. HOYT.

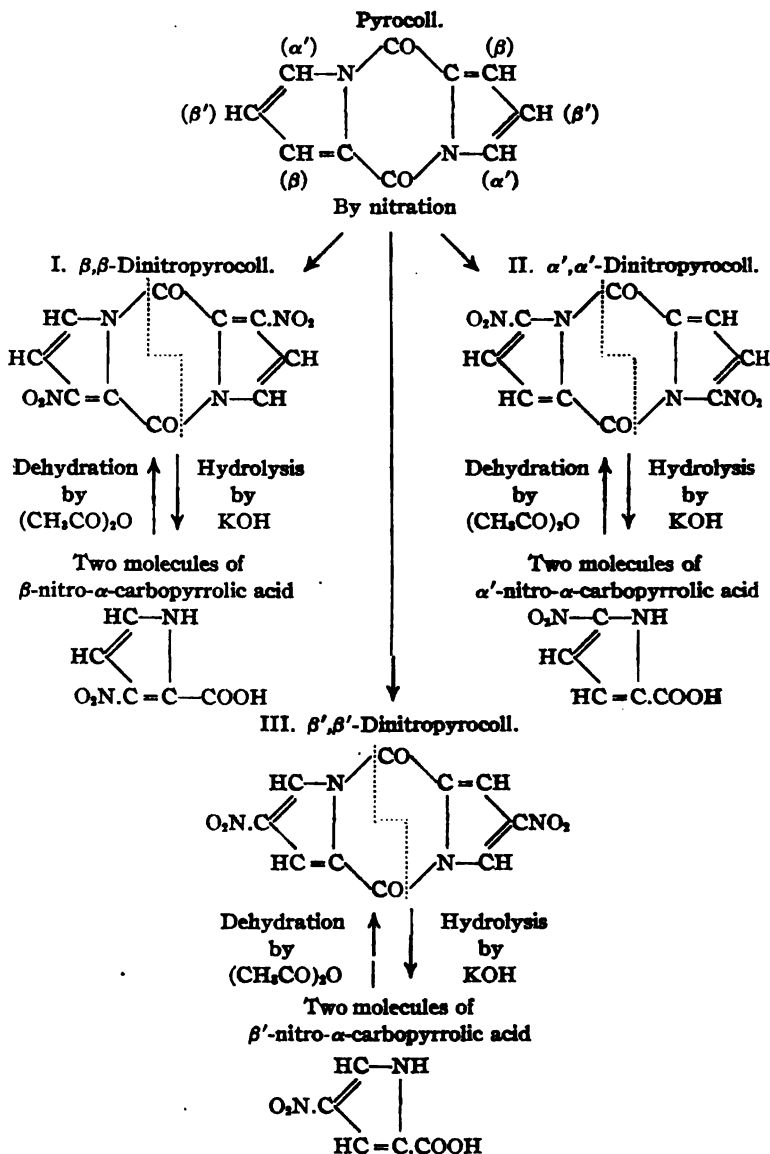
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The nitration of pyrocoll, as first reported by Ciamician and Danesi,¹ led to the formation of a dinitropyrocoll of unknown constitution. The hydrolysis of this dinitro derivative yielded a mononitro- α -carbopyrrolic acid in which the position of the nitro group still remained an undetermined factor. In a study of the constitution of each of the three possible mononitro- α -carbopyrrolic acids,² it was found that the method of Ciamician and Danesi was the only practical way of preparing this one acid just mentioned. Eventually, when we were able to establish the position of the nitro group for each of the three acids, this acid became identified as β -nitro- α -carbopyrrolic acid. The constitution therefore of the intermediate product—the unknown dinitropyrocoll—was then open for consideration and in similar manner each of the three possible symmetrical dinitropyrocrolls may be studied.

The production of this one β -nitro- α -carbopyrrolic acid in the absence of isomers when the unknown dinitropyrocoll is hydrolyzed (a fact noted also by Ciamician), has led us to the conclusion that, during this nitration of pyrocoll, two nitro groups apportion themselves equally and symmetrically upon the two pyrrole nuclei in the pyrocoll molecule. That configuration, therefore, for this dinitropyrocoll, which alone will satisfy this condition and, by hydrolysis, permit of the total conversion into two molecules of β -nitro- α -carbopyrrolic acid, is designated as sym. β, β -dinitropyrocoll.

¹ *Gazz. chim. ital.*, 12, 39 (1882).

² THIS JOURNAL, 37, 2538 (1915).



Further, in order to check this interpretation, we have reconverted the β -nitro- α -carbopyrrolic acid into this β, β -dinitropyrocoll of Ciamician and Danesi. The method was suggested by the known action of acetic anhydride upon α -carbopyrrolic acid, from which Ciamician and Silber¹ were able to prepare pure pyrocoll. In the case of β -nitro- α -carbopyrrolic

¹ Ber., 17, 103 (1884).

acid the condensation, in the presence of acetic anhydride, proceeded smoothly and gave an almost quantitative yield of β,β -dinitropyrocoll. The required temperature, that of boiling acetic anhydride, would indicate the initial formation of an acetyl derivative and the subsequent loss of acetic acid between two molecules of this product during the condensation into one molecule of β,β -dinitropyrocoll.

The nitration of pyrocoll, as described by Ciamician and Danesi, led no doubt in most cases to the formation of β,β -dinitropyrocoll. Slight alterations in the concentrations of nitric acid used and in the temperature at which nitration was conducted naturally may be expected to give widely varying results. Ciamician and Danesi employed fuming nitric acid cooled with ice. We, on the other hand, have found that the best conditions for the production of this same β,β -dinitropyrocoll are obtained when fuming nitric acid is reduced to a specific gravity of 1.50 and a constant temperature of $4-10^\circ$ is maintained. Under these conditions the nitration was found to proceed almost exclusively to the formation of β,β -dinitropyrocoll.

When the temperature of the nitric acid was considerably lowered, we were able to isolate from the reaction mixture a new isomer differing entirely from that dinitropyrocoll just described. The best conditions for the production of this second dinitropyrocoll consist in the use of an acid of the specific gravity of 1.6-1.7 and a constant temperature so low as -10° to -4° . The product thus obtained is never pure but more or less contaminated with a third dinitropyrocoll. These two new dinitropyrocolls can be separated by gentle warming with acetic acid in which the latter, or third isomer, is scarcely soluble. When thus separated the former, or second named isomer, is best purified by crystallization from acetic acid. It decomposes at $240-5^\circ$. The third isomer is produced in small quantity only, a 10% yield is usually the maximum, whereas the yield of the other two may exceed 60% of the theoretical value.

The second product, obtained as above, was hydrolyzed in the same manner as stated for the β,β -dinitropyrocoll. The acid obtained melted at 161° and proved to be identical in all respects with the acid prepared by Anderlini¹ (m. p. 161°), and lately² shown by us to possess the constitution of an α' -nitro- α -carbopyrrolic acid. By reason of the fact that this acid is the only product resulting from the hydrolysis just mentioned, and further by reason of its ready conversion, through the agency of acetic anhydride, into this same original dinitropyrocoll from which it was prepared, we are led to the conclusion that this second-named isomer of dinitropyrocoll is α',α' -dinitropyrocoll (II).

The third dinitropyrocoll, which, as has been stated, can be procured

¹ *Gazz. chim. ital.*, 19, 350 (1889).

² *THIS JOURNAL*, 37, 2545 (1915).

only in very small amounts is that product left undissolved in the glacial acetic acid used to remove the second isomer, or α',α' -dinitropyrocoll. It is best purified by crystallization from nitrobenzene. It is the most stable of the three forms, its decomposition taking place above 315° .

When hydrolyzed by alkali this dinitropyrocoll yielded an acid (m. p. 217°), which was found identical with that synthesized by us from nitromalonic aldehyde and glycine ester, and to which the constitution of a β' -nitro- α -carbopyrrolic acid must be assigned. This acid, prepared by either method, is readily converted by the action of acetic anhydride into the original dinitropyrocoll from which it alone results upon hydrolysis. The structure therefore of this third and last isomer of the symmetrical dinitropyrocolls must accord with that of a β',β' -dinitropyrocoll (III).

The study of the possible unsymmetrical dinitropyrocolls has not been undertaken. The nitration of pyrocoll leads primarily, if not exclusively, to the symmetrical dinitro derivatives. Though we may well have undertaken to synthesize the unsymmetrical derivatives by condensation between mixed acids, our interest lay primarily in the nitration of pyrocoll itself.

Experimental Part.

Preparation of Pyrocoll.—In a general way our method of preparation was the same as that described by Weidel and Ciamician.¹ 100 g. of commercial gelatin (preferably of low grade), were tightly compressed into a copper retort of about 750 cc. capacity. The retort cover was then clamped tightly upon the vessel. A slightly bent glass tube 1 meter long and 16 mm. diameter, to serve as a condenser, was now fitted into the 20 mm. opening in the retort cover and the joint tightly packed with shredded asbestos. It was found best to tilt the retort slightly toward the exit tube and to apply the full flame of a large Méker burner just behind the cover or exit. The tendency for the gelatin to foam out through the exit tube is thus avoided as all of the material in passing over the heated portion of the retort undergoes instant decomposition. After 15–20 minutes' heating oily drops begin to collect in the upper end of the condenser and at the same time pyrocoll distills over, condensing as a yellow crystalline product on the walls of the tube. The heating must be sufficiently rapid to insure complete decomposition and also to avoid the slow formation of ammonium salts, which are likely to be seen as a white crystalline deposit at the farther end of the condenser. On the other hand, a too rapid heating may easily lead to a choking of the delivery tube. When the decomposition of this amount of gelatin was complete, usually one hour's time, the contents of the tube were washed out with alcohol and the insoluble pyrocoll collected upon a filter. The yield amounted to

¹ *Monats.*, 1, 280 (1880).

0.5–0.6 g. for 100 g. of gelatin. The pyrocoll (m. p. 268°), was purified by crystallization from boiling glacial acetic acid.

β,β -Dinitropyrocoll, $C_{10}H_4O_2N_2(NO_2)_2$ (I).—This product is that which was obtained by Ciamician and Danesi,¹ in nitrating pyrocoll with fuming nitric acid. By hydrolysis with alkali he obtained from it the nitro- α -carbopyrrolic acid melting at 146°. The constitution of this acid, now known, establishes the constitution of this dinitropyrocoll as already discussed. The method employed by Ciamician and Danesi does not give uniform results, but leads to mixtures of all three of the possible dinitropyrocrolls. The following method, however, will give the best yield of this particular β,β -dinitropyrocoll with the smallest portions of the other two isomers.

Two grams of pyrocoll were added in about 0.1 g. portions to approximately 40 g. of nitric acid of 1.50 sp. gr. A temperature of 4 to 10° must be maintained throughout these additions. The pyrocoll dissolved readily with the attendant evolution of nitrogen tetroxide. When all of the pyrocoll was thus dissolved the dark brown liquid was gently warmed on the steam bath for a few moments, or until the evolution of the excess of nitric oxides had ceased. The red liquid was then poured into an excess of ice and water (150 cc.), whereupon a yellow noncrystalline product was precipitated. This product removed and dried upon a porous plate was treated with cold ethyl acetate which leaves undissolved the other dinitropyrocrolls possibly present. That product left upon the evaporation of the ethyl acetate was dissolved in hot glacial acetic acid, from which it crystallizes in fine yellow prisms, The yield amounts to about 60% of the theoretical quantity. This β,β -dinitropyrocoll is fairly soluble in acetic acid, nitrobenzene, acetone or ethyl acetate; slightly soluble in alcohol or benzene; and practically insoluble in ether, ligroin, chloroform or water. It dissolves to a considerable extent in cold ethyl acetate. Crystallization is best accomplished from a solution in nitrobenzene or glacial acetic acid. β,β -Dinitropyrocoll has no melting point but decomposes at 220–5°. When warmed with a 20% potassium hydroxide solution until a test portion fails to give a precipitate upon acidification with dilute sulfuric acid the hydrolysis of this dinitropyrocoll is complete, and from the original alkaline solution, when thoroughly cooled and acidified, extraction with ether will give the β -nitro- α -carbopyrrolic acid as previously described.

0.1191 g. subst. gave 22.3 cc. N_2 (24.7° and 748.4 mm. over H_2O).

Calc. for $C_{10}H_4O_2N_4$: N, 20.30. Found: N, 20.49.

If now this β -nitro- α -carbopyrrolic acid is dissolved in acetic anhydride and heated to boiling under a reflux condenser for one hour the resulting dark yellow solution, upon evaporation, is found to give the original β,β -dinitropyrocoll as anticipated.

¹ *Loc. cit.*

α',α' -Dinitropyrocoll, $C_{10}H_4O_2N_2(NO_2)_2$ (II).—No mention is made by Ciamician and Danesi¹ of having obtained even a trace of this isomer along with the dinitropyrocoll which they prepared. The following method for the nitration of pyrocoll was found to yield chiefly the α',α' -dinitropyrocoll. Two grams of pyrocoll were added in about 0.1 g. portions to about 40 g. of strong nitric acid of 1.6 to 1.7 sp. gr. A temperature of -10° to -4° must be maintained throughout this nitration. If the temperature should rise we naturally may expect a certain quantity of the β,β -dinitropyrocoll will be formed as in the preceding preparation. If the temperature falls too low the pyrocoll dissolves without attendant nitration and the subsequent dilution of the nitration mixture yields a tarry product of unknown composition. When the nitration was complete, according to the method just described, the red solution was warmed upon the water bath for a few minutes and then poured into about 150 cc. of ice water. The precipitate thus formed has a somewhat more voluminous appearance than the corresponding precipitate in the case of the β,β -dinitropyrocoll. After filtration the precipitate is dried upon a porous plate and treated with cold ethyl acetate to remove any traces of the β,β -dinitropyrocoll. It is next treated with glacial acetic acid, under gentle warming, and the solution concentrated, whereupon the α',α' -dinitropyrocoll crystallizes out in fine, yellow prisms. The yield is about 60% of the theoretical quantity. This α',α' -dinitropyrocoll is fairly soluble in acetic acid, nitrobenzene, or acetone; slightly soluble in alcohol, benzene, or ethyl acetate, and practically insoluble in ether, ligroin, chloroform, or water. It crystallizes best from acetic acid or nitrobenzene. It has no sharp melting point, but decomposes at $240-5^\circ$.

0.1406 g. subst. gave 26.2 cc. N_2 (24.3° and 746.6 mm. over H_2O).

Calc. for $C_{10}H_4O_2N_4$: N, 20.30. Found: N, 20.39.

When warmed with alkali α',α' -dinitropyrocoll is hydrolyzed in exactly the same manner as β,β -dinitropyrocoll but with the production in this case of α' -nitro- α -carbopyrrolic acid melting at 161° . This acid in turn when treated with boiling acetic anhydride is reconverted into the corresponding α',α' -dinitropyrocoll.

β',β' -Dinitropyrocoll, $C_{10}H_4O_2N_2(NO_2)_2$ (III).—In the nitration of pyrocoll, as described for the preparation of α',α' -dinitropyrocoll there is always found a variable amount of this third isomeric dinitropyrocoll. Scarcely any β',β' -dinitropyrocoll is produced in that nitration carried out primarily for the preparation of β,β -dinitropyrocoll. Consequently in the preceding preparation the product left after treatment with ethyl acetate, which removes any traces of β,β -dinitropyrocoll, is next treated with warm glacial acetic acid, in which α',α' -dinitropyrocoll is quite soluble. The residue left after this second process of extraction is practically pure

¹ *Loc cit.*

β',β' -dinitropyrocoll. This latter is only sparingly soluble in hot glacial acetic acid and when so dissolved may be crystallized out in fine, yellow prisms. It is best however to crystallize it from nitrobenzene, in which it is more soluble. β',β' -Dinitropyrocoll is fairly soluble in nitrobenzene or acetone; slightly soluble in acetic acid, alcohol, benzene, or ethyl acetate, and practically insoluble in ether, ligroin, chloroform or water. It decomposes without melting at $315-20^\circ$. Upon hydrolysis with strong alkali, in the same manner as directed for the preceding dinitropyrocolls, this product yielded β' -nitro- α -carbopyrrolic acid, melting at 217° . And again by the action of acetic anhydride this latter is most readily converted into the original β',β' -dinitropyrocoll.

0.1392 g. subst. gave 0.2211 g. CO_2 and 0.0225 g. H_2O ; 0.1734 g. subst. gave 32.8 cc. N_2 (25.5° and 741.3 mm. over H_2O).

Calc. for $\text{C}_{10}\text{H}_4\text{O}_4\text{N}_4$: C, 43.46; H, 1.46; N, 20.30. Found: C, 43.33; H, 1.81; N, 20.42.

Since β' -nitro- α -carbopyrrolic acid is that particular acid which is easily synthesized from glycine ester and nitromalonic aldehyde,¹ its preparation by the nitration of pyrocoll is not to be advised. Furthermore, the nitration of pyrocoll with this acid in view has never yielded more than 10% of the theoretical quantity. It should be stated further that a small amount of this β',β' -dinitropyrocoll is also usually found in the product obtained from the nitration of pyrocoll according to the method of Ciamician and Danesi. In this connection we wish to express our indebtedness to Mr. E. M. Honan, of this laboratory, for the care he has taken in checking our results.

ANN ARBOR, MICH.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF VANDERBILT UNIVERSITY.]

THE REACTION BETWEEN ALCOHOLS AND AQUEOUS SOLUTIONS OF HYDROCHLORIC AND HYDROBROMIC ACIDS.

BY JAMES F. NORRIS, MURIEL WATT AND RUTH THOMAS.

Received February 28, 1916.

In a previous paper² it was shown that a large number of aliphatic and aromatic alcohols react with aqueous solutions of hydrobromic acid and hydriodic acid and form the corresponding organic bromides and iodides, and that, in certain cases, analogous reactions take place with hydrochloric acid. When the alcohols and the constant-boiling mixtures of the acids and water were distilled, good yields of the halides were obtained. The substances formed in this way were free from the impurities which are present when phosphorous compounds are used to prepare them. The method has been used when especially pure halides

¹ *Loc. cit.*

² *Am. Chem. J.*, 38, 627 (1907).

have been required for investigation,¹ and it has found its way into laboratory guides.² On account of the fact that the method has proved to be a valuable one in certain cases, it seemed advisable to study the behavior of a greater variety of alcohols with aqueous solutions of hydrochloric acid and hydrobromic acid. Up to the present no work, in addition to that already published, has been done with hydriodic acid, since in all the cases studied it was found that hydriodic acid behaved in the same way as hydrobromic acid; the only difference observed was that slightly better yields were obtained with the former acid. Alcohols were selected for study to throw light on the following points: the effect of structure on the readiness with which the reaction takes place, the cause of the difference between the behavior of hydrochloric acid and that of hydrobromic acid, the value of hydrobromic acid as a reagent to test for an alcoholic hydroxyl group, and, finally, the applicability of the reaction as a general preparative method for alkyl halides.

The effect of the structure of the alcohol on its reactivity is marked. The rate at which primary alcohols react with aqueous hydrobromic acid (sp. gr. 1.49) decreases, in general, with increase in molecular weight. The alcohol with the highest molecular weight studied was cetyl alcohol; a yield of 72% of bromide was obtained after heating for four hours a mixture of the alcohol and acid in the molecular proportion of one of the former to four of the latter.

The conclusion drawn from the previous work on primary, secondary, and tertiary alcohols, namely, that the ease of reaction increases in the above order, was confirmed.

A study of the difference between the behavior of hydrochloric acid and hydrobromic acid brought out some interesting results, which will be the subject of further study, since no satisfactory reason is yet evident for the great difference in the behavior of these two acids. It was shown in the previous paper that benzyl alcohol reacted readily with aqueous hydrochloric acid, whereas ethyl alcohol did not. The replacement of the methyl radical by phenyl brought about this difference. A study of a number of primary saturated aliphatic alcohols has been made; none reacts with aqueous hydrochloric acid when heated in an open vessel. The influence of the presence of a phenyl radical in an alcohol is marked. To determine the effect of the position of this radical on the behavior of the alcohol with hydrochloric acid, alcohols of the following structures were

¹ See Michael, *Ann.*, 379, 291 (1911) and 393, 95 (1912). Michael found that in the case of some of the higher alcohols the bromides prepared by him from alcohols and aqueous hydrobromic acid contained small quantities of unsaturated hydrocarbons; the latter were removed by shaking the halide with a dilute solution of potassium permanganate. In order to avoid the formation of by-products, the reaction should be carried out at as low a temperature as possible.

² See "Practical Organic Chemistry," Sudborough and James; Van Nostrand.

studied under the same conditions: $C_6H_5CH_2OH$, $C_6H_5CH_2CH_2OH$, and $C_6H_5CH_2CH_2CH_2OH$. Benzyl alcohol was readily converted into benzyl chloride in the cold by concentrated hydrochloric acid, and when distilled with acid of the specific gravity 1.1 gave a good yield of the chloride. Primary phenylethyl alcohol gave but a trace of the chloride, and there was no reaction with the derivative of propyl alcohol.

Since the phenyl radical is negative, it seemed possible that an aliphatic radical more negative than methyl or ethyl if joined to the carbinol carbon, might produce an effect similar to that of the aryl radical. Accordingly, the behavior of allyl alcohol, $CH_2 = CH.CH_2OH$, with hydrochloric acid (sp. gr. 1.1) was studied. In this case the vinyl radical, which has a negative nature due to the double bond, replaces the phenyl radical of benzyl alcohol. When allyl alcohol was distilled with a large excess of the constant-boiling mixture of hydrochloric acid and water, a yield of 50% of allyl chloride was obtained. It is interesting to note in this connection that the ionization constant of benzoic acid, $C_6H_5.COOH$, is 0.0060, and that of acrylic acid, $CH_2 = CH.COOH$, is 0.0056. The phenyl radical and the vinyl radical have approximately the same effect on the ionization of the acids made up of these radicals and the carboxyl group; they have thus approximately the same electronegative character. It is probable that this character is a determining factor in the behavior of compounds containing these groups; the similarity of the reactivity of benzyl alcohol and allyl alcohol is an example. The behavior of other substances which contain the vinyl radical resembles markedly that of compounds of analogous structure containing the phenyl radical. This important fact is being investigated further.

As has been stated above, there was no chloride formed from primary phenylpropyl alcohol, $C_6H_5CH_2CH_2CH_2OH$, and hydrochloric acid; cinnamyl alcohol, $C_6H_5CH = CHCH_2OH$, on the other hand, gave a yield of 80% of the chloride when distilled with aqueous hydrochloric acid (sp. gr. 1.1). The results with the aromatic alcohols and with the two unsaturated alcohols bring out the important fact that the reactivity of alcohols with hydrochloric acid is facilitated by the accumulation of negative radicals around the carbinol carbon atom. If the reaction between an alcohol and an acid is similar to that between a base and an acid, it appears that the accumulation of negative radicals increases basicity. This point of view, which seems far from reasonable at first sight, is not necessarily false. It is possible that the proper balance of the so-called negative radicals may produce the behavior which we associate with positive radicals. The case of the iodonium compounds is an example; by the union of two negative phenyl radicals with an iodine atom, we obtain a group $(C_6H_5)_2I$, which has marked basic properties, since diphenyliodonium hydroxide $(C_6H_5)_2I.OH$, is a comparatively strong base.

Recent work on the base-forming property of oxygen brings out the fact that when radicals containing double bonds are linked to oxygen the resulting compounds show a greater basicity than those containing saturated radicals. Since radicals containing double bonds are more negative than the corresponding saturated ones, the results indicate that increase to a certain degree in the negativity of the substituents in a molecule increases the basicity or positive character of the group made up of these radicals. Experiments which have been carried out to test this view indicate that the basicity of alcohols can be increased by grouping negative radicals around the carbinol carbon atom.

It is possible that the reaction between an alcohol and an acid is not of the same nature as that between an inorganic base and an acid. Experiments are now in progress to bring additional light on this important question. It is highly probable that other factors than those of positivity and negativity are of importance in the reactions studied. The experiments in progress include a search for these factors.

In order to study further the effect of the nature of the radicals present in an alcohol on its reactivity with hydrochloric acid, the three nitrobenzyl alcohols were investigated. In no case was the hydroxyl group replaced by chlorine. The introduction of the nitro group into the phenyl radical markedly increases its negativity, since the ionization constants of the nitrobenzoic acids are much greater than that of benzoic acid. It is evident, therefore, that if the negativity of a group is a factor in determining the basicity of an alcohol, there are limits in the negativity, between which the highest degree of basicity is produced. The effect of the nature of radicals on basicity is being studied from this point of view.

It was stated above that increase in molecular weight in the paraffin series decreases the activity of the alcohol and that secondary alcohols react more readily than primary alcohols. Secondary butyl alcohol formed a chloride with hydrochloric acid, but secondary octyl alcohol did not. The effect of increased molecular weight in this case overcame the effect of the secondary structure.

All the alcohols studied formed bromides when heated with the constant-boiling mixture of hydrobromic acid and water. Since 27 aliphatic and aromatic alcohols, which vary markedly in structure, have been studied, it seems that the reaction can be advantageously used as a reliable qualitative test for an alcoholic hydroxyl group in monatomic alcohols. Aqueous hydriodic acid reacts with certain esters and ethers, and, as a consequence, cannot be used in testing for the presence of alcoholic hydroxyl. It seemed desirable, therefore, to determine if aqueous hydrobromic acid reacted in an analogous way. The acid did not convert ether or ethyl acetate into ethyl bromide when the substances were distilled together. It is probable, therefore, that ethers and esters which

behave normally will not react with hydrobromic acid under the conditions to be used in the test for the hydroxyl group, namely, heating the substance to be investigated in an open vessel with the constant-boiling aqueous solution of hydrobromic acid. It is probable that in certain cases hydrobromic acid is a better reagent for alcoholic hydroxyl than acetyl chloride, or acetic anhydride, since these substances react at times with acidic hydroxyl.

The statements above refer to monatomic alcohols. A study has been begun of the behavior of polyatomic alcohols with hydrobromic acid. Glycol was in part converted into ethylene bromide, and glycerol into a bromohydrin. The yields in both cases were small. Details of the reactions are given in the experimental part of the paper.

Since in all the cases of monatomic alcohols studied good yields of bromides and iodides were obtained, the reactions can be advantageously used to prepare these compounds. In this paper no work on hydriodic acid is reported, but as has been stated, the reactions with this acid take place more readily than with hydrobromic acid, and it is highly probable that iodides could be prepared from the alcohols whose behavior with hydrobromic acid is described below.

Experimental Part.¹

In the paper to which reference has been made a description was given of the action of hydrochloric, hydrobromic and hydriodic acids on the alcohols containing the following radicals: methyl, ethyl, propyl, isopropyl, isobutyl, secondary butyl, tertiary butyl, isoamyl, allyl, benzyl, diphenylmethyl, triphenylmethyl and tritolylmethyl. In this paper are given the results of the study of the alcohols containing the following radicals: allyl, tertiary amyl, heptyl (pentamethylethanol), normal octyl, secondary octyl, cetyl, ortho-, meta-, and paranitrobenzyl, primary phenylethyl, primary phenylpropyl and cinnamyl. Glycol and glycerol were also studied.

Allyl Alcohol.—The alcohol was mixed with varying quantities of hydrochloric acid and slowly distilled. The highest yields of chloride were obtained when the constant-boiling mixture of the acid and water was used. With concentrated hydrochloric acid a higher percentage of alcohol distilled over unchanged than when the solution of acid containing 20.2% hydrogen chloride was used. A series of experiments showed that the highest yield was obtained when 1 g. molecule of the alcohol was distilled with 5 g. molecules of the constant-boiling mixture of hydrogen chloride and water. Under these conditions 10 g. of allyl alcohol and 160 g. of hydrochloric acid (sp. gr. 1.1), gave 7 g. of allyl chloride. After drying and distillation the yield was 50% of the theoretical. The yields were practically the same when 10 and 20 g. molecules of acid were used.

¹ The work described was done in the laboratory of Simmons College.

The yields of allyl bromide (61%) and allyl iodide (58%), reported in the previous paper were obtained with the commercial alcohol. When the pure alcohol was used under the same conditions, 1 molecule of alcohol to 3 molecules of the constant-boiling acids, the yield of bromide was found to be practically the theoretical; the yield of iodide was 84%.

Tertiary Amyl Alcohol.—When 5 g. of the alcohol were distilled with 29 g. of hydrobromic acid (sp. gr. 1.49) (molecular ratio 1 : 3), the yield of tertiary amyl bromide was 95% of the theoretical. When the constant-boiling mixture of hydrochloric acid and water was used in the same molecular ratio, the yield of chloride was 93%; under the same conditions with concentrated hydrochloric acid the yield was 98% of the theoretical.

Normal Octyl Alcohol.—With increasing molecular weight the reaction between the alcohols and hydrobromic acid took place more slowly. In order to increase the yield of halide the alcohol was accordingly boiled with the acid in a flask provided with a reflux condenser. A large excess of acid was required to produce satisfactory yields. When 5 g. of normal octyl alcohol were heated for one hour with 25.5 g. of hydrobromic acid (four times the theory), 3.5 g. of the bromide were obtained. When the same molecular proportions were used and the mixture heated two hours, 10 g. of the alcohol gave 10 g. of bromide, which is 66% of the theoretical. The alcohol which distilled unchanged with the bromide was removed by shaking the mixture with ice-cold concentrated sulfuric acid. The bromide was then washed with water, dried over calcium chloride and distilled. The bromide boiled at 201–202° (corrected).

Secondary Octyl Alcohol.—Ten grams of the alcohol were heated for 2 hours with 51 g. of hydrobromic acid (molecular ratio 1 : 4). The bromide was purified as described above. The yield of bromide boiling at 188–189° (corrected), was 60% of the theoretical.

When the alcohol was boiled with hydrochloric acid only a trace of chloride was formed.

Pentamethylethanol, $(\text{CH}_3)_3\text{C}.\text{C}(\text{CH}_3)_2.\text{OH}$.—Since tertiary butyl alcohol reacts much more readily with acid than normal butyl alcohol, the compound of the structure given above was prepared and studied. It has the tertiary structure and, in addition, a tertiary butyl radical. It was thought that the alcohol might show more base-like properties than any alcohol yet investigated. The compound was prepared from pinacoline and methyl iodide by the method described by Henry.¹ The yields in two preparations were 68% and 75%. The alcohol was converted in the cold by hydrobromic acid into the bromide. The reaction took place slowly, since both the alcohol and bromide are insoluble in the acid. It was found difficult to separate the alcohol from the bromide, as both

¹ *Rec. trav. chim.*, 26, 84 and 106 (1907).

sublime at low temperatures. The extent to which the reaction took place between the alcohol and acid was determined by titrating the acid which was left over after reaction had taken place. Since the basicity of this alcohol appeared to be greater than that of any of the others studied, the extent to which reaction took place between equal molecular quantities of the alcohol and hydrobromic acid diluted with water was investigated. The constant-boiling mixture of hydrobromic acid and water contains its constituents approximately in the ratio of 1 of the acid to 5 of water. When pentamethylethanol, hydrogen bromide, and water in the molecular ratio 1 : 1 : 7.5, respectively, were allowed to react at room temperature, 16% of the alcohol was converted into bromide; when the mixture was heated at 60° for ten minutes the percentage of bromide formed was increased to 25. When tertiary butyl alcohol was studied under the same conditions the results were approximately the same. Since the alcohol did not possess basic properties markedly greater than those of tertiary butyl alcohol, it was not investigated further.

Cetyl Alcohol.—Ten grams of the alcohol were heated with 33 g. of constant-boiling hydrobromic acid (molecular ratio 1 : 5) for four hours. The product was separated and extracted with hot alcohol, which dissolved out the alcohol which had not reacted. The weight of the bromide formed was 9.5 g., which is 80% of the theoretical.

***o*-Nitrobenzyl Alcohol.**—Hydrochloric acid did not convert the alcohol into the chloride. When 1 g. of the alcohol was slowly heated in a water bath with 3.3 g. of hydrobromic acid (sp. gr. 1.49), the alcohol dissolved when the temperature was 50°. At 75° the solution clouded and the bromide separated slowly. After heating 1.5 hours, the product was separated, washed with concentrated hydrochloric acid to remove any unchanged alcohol. The bromide obtained melted at about 39°; after recrystallization from a mixture of alcohol and water the melting point was 46–47°. The yield of pure bromide was 85% of the theoretical. An analysis for halogen gave 36.79% bromine; the theoretical is 37.03%.

***m*-Nitrobenzyl Alcohol.**—The alcohol was not converted into the chloride by hydrochloric acid. When 1 g. of the alcohol was heated on a water bath with 3.3 g. of hydrobromic acid the bromide began to separate at 83°; after heating for 1.5 hours the bromide was separated and weighed. The yield was 64% of the theoretical. The bromide melted at 58–59°, which is the recorded melting point.

***p*-Nitrobenzyl Alcohol.**—The alcohol was not converted into the chloride when heated with hydrochloric acid. When 1 g. of the alcohol was heated with 3.3 g. of hydrobromic acid the bromide began to separate at about 85°. After heating 1.5 hours the product was separated, washed with concentrated hydrochloric acid, and dried. The yield of bromide, which melted at 99–100°, was 1.4 g., 99% of the theoretical.

Primary Phenylethyl Alcohol, $C_6H_5CH_2CH_2OH$.—Ten grams of the alcohol were heated with 75 g. of hydrochloric acid (sp. gr. 1.1) (molecular ratio 1 : 5) for 2 hours. The product was separated and distilled. A very small amount of the chloride was obtained. Five grams of the alcohol were slowly distilled with 28 g. of hydrobromic acid (molecular ratio 1 : 4). The product was washed with hydrochloric acid, dried, and distilled. The bromide boiled at 108–112° at 17 mm. pressure. The yield was 86% of the theoretical.

Secondary Phenylethyl Alcohol, $C_6H_5CH_2CH_2CHOH$.—Five grams of the alcohol were distilled with 74 g. of constant-boiling hydrochloric acid (molecular ratio 1 : 10). The product was separated, dried and distilled. It was evident from the irregular boiling point of the chloride that a secondary reaction had taken place. It is probable that as a result of the long heating an unsaturated hydrocarbon had been formed in appreciable quantities. To avoid this the alcohol was shaken at room temperature with the acid. Ten grams of the alcohol and 75 g. of hydrochloric acid (sp. gr. 1.1) were shaken vigorously for about ten minutes. The product was separated, dried, and distilled under diminished pressure. Eight grams of the chloride, which boiled at 90–91° at 33 mm. pressure, were obtained. The yield of pure chloride was about 75% of the theoretical. Five grams of the alcohol were distilled with 28 g. of the constant-boiling hydrobromic acid (molecular ratio 1 : 4). The bromide obtained distilled at 106° at 31 mm. pressure. The yield was 95% of the theoretical.

Primary Phenylpropyl Alcohol, $C_6H_5CH_2CH_2CH_2OH$.—When the alcohol was boiled with hydrochloric acid a product which did not boil constantly was obtained. It is probable that the mixture contained an unsaturated hydrocarbon. No chloride was isolated. Ten grams of the alcohol were heated for two hours with 22 g. of hydrobromic acid (molecular ratio 1 : 2). The product, after washing and drying, was distilled under diminished pressure. Eight grams of bromide were obtained, which boiled at 128–129° (corrected) at 29 mm. The yield was 63% of the theoretical.

Cinnamyl Alcohol.—Five grams of the alcohol were distilled with 33.5 g. of constant-boiling hydrochloric acid (molecular ratio 1 : 5). The product was solidified by cooling, filtered, and washed. It was then melted and filtered twice through dry filter paper. A clear oil was obtained which melted at 4–9°. The recorded melting point was 8–9°. It contained 23.37% chlorine; the theoretical is 23.27%. The yield of chloride was 79% of the theoretical.

Five grams of the alcohol were distilled with 19.5 g. of hydrobromic acid (molecular ratio 1 : 3). The product was treated in the manner used to purify the chloride. It melted at 18–23°, and decomposed when boiled.

The yield was 93% of the theoretical. The percentage of bromine formed was 40.14; the theoretical percentage is 40.61.

Glycol.—Ten grams of the alcohol were heated 2 hours with 145 g. of constant-boiling hydrochloric acid (molecular ratio 1 : 5). The mixture was then fractionated; neither ethylene chloride nor the chlorohydrin were obtained. Twenty grams of glycol were boiled for 2 hours with 165 g. of hydrobromic acid (molecular ratio 1 : 3). The mixture was then fractionated, using a Glinsky tube. No bromohydrin was obtained, but there were formed 8 cc. of an insoluble oil which proved to be ethylene bromide, the yield being 36% of the theoretical. In another experiment when the mixture was heated for a shorter time, some of the bromohydrin was obtained. The exact conditions which determine replacement of one and two hydroxyl groups by bromine were not determined.

Glycerol.—A mixture of 10 g. of glycerol and 55 g. of hydrobromic acid (molecular ratio 1 : 3) was distilled slowly at ordinary pressure until the temperature of the vapor was 140°. The distillation was continued at 33 mm. pressure. The product obtained boiled at 146–175°. After three fractionations at 30 mm. pressure 6 g. of an oil which boiled at 145–147° (corrected) were obtained. The bromohydrins have not been carefully studied. It is probable that the compound obtained was identical with that described by Veley,¹ who prepared it by passing hydrogen bromide into glycerol. The boiling point recorded is 160° at 66 mm.

NASHVILLE, TENN.

HALOGENATION. X. CHLORIC ACID AS A REAGENT IN ORGANIC CHEMISTRY.

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The preparation of organic chlorates has not been attempted with the exception of a few isolated instances. It was thought desirable to study the chlorates of organic bases systematically, as also the action of chloric acid on organic compounds in general.

Chlorates have been prepared either by the direct action of chloric acid on the organic base or by means of double decomposition between the hydrochloride of the base and silver chlorate. They form readily with the aliphatic bases according to either of the above methods, but in the case of aromatic bases the action is quite different. Sometimes the chlorate could not be formed at all since the base undergoes oxidation rapidly. With an excess of chloric acid, the decomposing bases form brown to yellow oily substances which consist, generally, of the lower chloroquinones. With regulated amount of chloric acid, the decomposing substances form dyes. It has also been found that iodo derivatives of

¹ *Jahresbericht d. Chemie*, 1883, 838.

aromatic hydrocarbons readily form iodoxy compounds when subjected to its prolonged action.

Chlorates are, as a rule, either explosives or highly unstable in the dry state, and special precautions must therefore be taken to determine their melting or decomposition point. Not all explode, however, some melting quite harmlessly and some with more or less decomposition. When held in a flame or touched with a drop of concentrated sulfuric acid, these chlorates burn off suddenly, in some cases with production of a sharp report. Chlorates of aromatic bases sometimes go off spontaneously, specially if the chlorate has been obtained by the direct action of chloric acid on the base, probably as the result of a little free chloric acid which might be present. Such spontaneous explosion does not take place if the chlorate be purified by recrystallization from alcohol.

The analysis of these chlorates is carried out by mixing with a large quantity of powdered copper oxide.

Experimental.

Action of Chloric Acid on Aniline.—Aniline chlorate has been prepared before by direct neutralization.¹ It has been found that when aniline is mixed with quite an excess of chloric acid, a vigorous reaction, with the evolution of a considerable amount of heat, takes place and as a result of the action a brown oil is formed which settles at the bottom. The oil consists of a mixture of the lower chloroquinones which is under examination. But if a little chloric acid is added to an excess of aniline and the mixture allowed to stand at the ordinary temperature, it undergoes gradual oxidation and finally a black substance is precipitated. This has been found on examination to be aniline black, giving all its reactions. (Found, N = 15.48; calc., N = 15.34.) The yield obtained is quantitative.

o-Toluidine Chlorate, $C_7H_7N.HClO_3$.—To an excess of o-toluidine, chloric acid is added drop by drop, when crystals begin to make their appearance. Care is taken not to add an excess of chloric acid, as the presence of a little free acid will decompose the substance explosively at ordinary temperature, a slight excess of toluidine being maintained. The crystals are filtered with suction, washed thoroughly with ether and benzene, and finally recrystallized from alcohol when it is obtained in white plates.

0.1642 g. gave 0.2652 g. CO_2 and 0.0735 g. H_2O ; 0.0594 g. gave 4.1 cc. N_2 at 28° and 763 mm.; 0.1435 g. gave 0.1068 g. AgCl.

Calc. for $C_7H_7N.HClO_3$: C, 43.86; H, 5.22; Cl, 18.5. Found: C, 43.77; H, 5.25; N, 7.6; Cl, 18.63%.

The crystals are not indefinitely stable in air, but turn gray and finally produce a black substance which, as will be shown later, is also formed

¹ Beamer and Clarke, *Ber.*, 12, 1066 (1879); Gerard, *L'Hôte, Ann.*, [6] 22, 404.

by the prolonged action of chloric acid on *o*-toluidine. *o*-Toluidine chlorate explodes at 88°. When a flame is applied to it, it burns explosively.

It has also been found that on adding an excess of chloric acid to a little *o*-toluidine, a blue-colored solution is produced and the mixture becomes hot. This is followed by a vigorous reaction, with boiling, and a brown-black viscous liquid separates at the bottom. This substance is under examination.

If an excess of *o*-toluidine is left in contact with chloric acid and the vessel cooled with water so as to avoid any vigorous reaction, the toluidine is slowly transformed into a black insoluble substance which gives some of the tests of *o*-toluidine black. The dye has been found to be quite distinct from *o*-toluidine black and is under systematic examination. The same dye is obtained by the gradual decomposition in air of *o*-toluidine chlorate, as has been already noticed.

***p*-Toluidine Chlorate, $C_7H_7N.HClO_3$.**—For the preparation of this compound *p*-toluidine is dissolved in ether and to it an aqueous solution of chloric acid is added drop by drop, taking care to keep the *p*-toluidine in slight excess. The ether is then allowed to evaporate at the ordinary temperature as rapidly as possible. As the ether evaporates, long, white crystals remain behind. The crystals are washed with ether and benzene and finally recrystallized from alcohol.

0.2110 g. gave 0.3405 g. CO_2 and 0.0993 g. H_2O ; 0.0594 g. gave 3.85 cc. N_2 at 26° and 764 mm.; 0.1552 g. gave 0.1157 g. $AgCl$.

Calc. for $C_7H_7N.HClO_3$: C, 43.86; H, 5.22; N, 7.32; Cl, 18.54. Found: C, 43.22; H, 5.33; N, 7.33; Cl, 18.78.

p-Toluidine chlorate explodes at 125°, giving off a large amount of white fumes and takes fire suddenly when a flame is applied to it. The substance on exposure to air gradually turns gray owing to slow decomposition of the salt.

Similarly to *o*-toluidine, it has been found that on treating *p*-toluidine with an excess of concentrated chloric acid, a vigorous reaction begins in the course of an half-hour with considerable evolution of heat and as a result of the reaction a brown viscous oil, which is under examination, settles at the bottom. But if an excess of *p*-toluidine be kept with a little dilute solution of chloric acid in the cold, the mixture gradually turns black and the *p*-toluidine is ultimately converted into a black dye. The dye is under examination.

***p*-Phenylenediamine Chlorate.**—Chloric acid, when added directly to *p*-phenylenediamine, dissolves it and gives a deep blue solution which gradually assumes a brown color. If an ethereal solution of the diamine is mixed with chloric acid on a watch glass and the ether is allowed to evaporate rapidly, crystals are obtained. They could hardly be separated

for purification as the material soon turns black. The same black dye is obtained when *p*-phenylenediamine is left in contact with chloric acid in the cold. The systematic investigation of the dye is in progress.

An attempt was made to obtain *m*-phenylenediamine chlorate by double decomposition between *m*-phenylenediamine hydrochloride and silver chlorate. The resulting solution began to turn dark as soon as double decomposition was complete. On allowing the solution to evaporate in a vacuum, instead of the chlorate, a gray-black dye is left behind. The further examination of this black substance is in progress.

Benzylamine Chlorate, $C_7H_9N.HClO_3$.—For the preparation of the chlorate an excess of benzylamine is mixed with an aqueous solution of chloric acid. The resulting solution is allowed to evaporate on the water bath and the product remains melted over it. On cooling, the liquid solidified in nice crystalline plates which are slightly yellow in color owing to the presence of benzylamine. To free it from benzylamine, it is washed thoroughly with ether and finally purified by recrystallization from alcohol.

0.1825 g. gave 0.2934 g. CO_2 and 0.0856 g. H_2O ; 0.0730 g. gave 4.75 cc. N_2 at 23° and 765 mm.

Calc. for $C_7H_9N.HClO_3$: C, 43.86; H, 5.22; N, 7.32. Found: C, 43.83; H, 5.62; N, 7.6%.

Benzylamine chlorate melts at 110.5° to a yellow liquid. It is hygroscopic and dissolves in water and alcohol but not in ether and benzene.

Benzylmethylamine Chlorate, $C_8H_{11}CH_2NHCH_3.HClO_3$.—Equivalent quantities of benzylmethylamine and chloric acid are mixed with a slight excess of the former. The mixture is first heated on the water bath for about an hour and is then allowed to cool in a desiccator. The solid mass thus obtained is then washed thoroughly with ether and recrystallized from alcohol and dried.

0.1405 g. gave 0.2352 g. CO_2 and 0.0674 g. H_2O ; 0.1038 g. gave 6.3 cc. N_2 at 23° and 762 mm.

Calc. for $C_8H_{11}N.HClO_3$: C, 46.7; H, 5.84; N, 6.81. Found: C, 45.52; H, 5.99; N, 7.02%.

The chlorate melts at 59.60°. It is soluble in water and alcohol but not in ether and benzene. It burns off suddenly when a flame is brought near to it.

Benzylethylamine Chlorate, $C_8H_9CH_2.NHC_2H_5.HClO_3$.—Equivalent amounts of benzylethylamine and chloric acid are mixed and heated on the water bath for some time. On cooling, crystals separate which are thoroughly washed with ether and recrystallized from dilute alcohol.

0.1010 g. gave 0.3626 g. CO_2 and 0.1052 g. H_2O ; 0.1588 g. gave 8.85 cc. N_2 at 24° and 763 mm.

Calc. for $C_8H_{11}N.HClO_3$: C, 49.2; H, 6.38; N, 6.38. Found: C, 49.19; H, 6.55; N, 6.33.

The chlorate melts at 81.5° . It takes fire suddenly when a flame is applied to it. It is very soluble in water and alcohol but insoluble in ether and benzene.

Piperazine Chlorate, $C_4H_{10}N_2 \cdot 2HClO_3$.—Piperazine chlorate is prepared by double decomposition between silver chlorate and piperazine hydrochloride. On evaporation of the solution in a vacuum over sulfuric acid, the chlorate is obtained in nice, white, shining crystalline plates. On presenting a flame to it, it takes fire suddenly. It decomposed between 98 and 100° . In this case the decomposition was not explosive.

0.2215 g. gave 22.2 cc. N_2 at 24° and 760 mm.; 0.1234 g. gave 0.1378 g. AgCl.

Calc. for $C_4H_{10}N_2 \cdot 2HClO_3$: N, 10.98; Cl, 27.8. Found: N, 11.22; Cl, 27.91.

Ethylenediamine Chlorate, $C_2H_4(NH_2)_2 \cdot 2HClO_3$.—This chlorate is prepared by neutralizing ethylenediamine solution with chloric acid by the help of a litmus paper and evaporating the resulting solution on the water bath to crystallization where the substance is obtained in shining, white, flat crystals. As thus obtained, it is quite pure and a single recrystallization from water or alcohol gives a very pure product. It decomposes at 150° . Like the other chlorates, it burns off with a flash on presenting a flame to it.

0.1825 g. gave 19.85 cc. N_2 at 25° and 760 mm.; N, 12.34.

Calc. for $C_2H_4(NH_2)_2 \cdot 2HClO_3$: N, 12.23.

Guanidine Chlorate, $CN_3H_5 \cdot HClO_3$.—This is obtained by the double decomposition between guanidine sulfate and barium chlorate and evaporating the resulting solution over a water bath, when white crystals are obtained. It decomposes at 148° and does not explode sharply at that temperature. However, it burns away on presenting a flame to it or touching with a drop of concentrated sulfuric acid.

0.1010 g. gave 26.3 cc. N_2 at 23° and 767 mm.

Calc. for $CN_3H_5 \cdot HClO_3$: N, 29.8. Found: 30.62.

Menthylamine Chlorate, $C_{10}H_{19}NH_2 \cdot HClO_3$.—This has been prepared by the double decomposition between menthylamine hydrochloride and silver chlorate and evaporating the solution in a vacuum over sulfuric acid. The chlorate is then left in beautiful, white, crystalline needles. It melts at 168° . This chlorate, unlike the previous ones, does not flash off when a burning stick is brought near it but it simply melts.

0.0828 g. gave 4.4 cc. N_2 at 24° and 762 mm.; N, 6.07.

Calc. for $C_{10}H_{19}NH_2 \cdot HClO_3$: N, 5.85.

Pyridine Chlorate, $C_5H_5N \cdot HClO_3$.—When a slight excess of pyridine is mixed with concentrated chloric acid and the mixture is heated on the water bath, crystals of the chlorate are left. They are washed with water and recrystallized from alcohol, and then melt with decomposition at 147° .

0.1021 g. gave 7.6 cc. N_2 at 23° and 766 mm.; 0.1827 g. gave 0.1592 g. AgCl.
Calc. for $C_5H_5N.HClO_3$: N, 8.56; Cl, 21.7. Found: N, 8.58; Cl, 21.92.

Pyridine chlorate burns with a sudden flash. It also takes fire when concentrated sulfuric acid is allowed to come in contact with it. It is soluble in water and alcohol but does not dissolve in nondissociating organic solvents. The crystals are soft and soapy to the touch and give the odor of pyridine.

Quinoline Chlorate, $C_9H_7N.HClO_3$.—This has been prepared by mixing chloric acid with rather more than the theoretical amount of quinoline and evaporating on the water bath. The crystals obtained are washed with a mixture of alcohol and ether for purification. The compound melts at $66-67^\circ$.

0.1117 g. gave 6.65 cc. N_2 at 25° and 760 mm.
Calc. for $C_9H_7N.HClO_3$: N, 6.56. Found: N, 6.76.

The chlorate has a slightly yellowish tinge and is very hygroscopic. It is soluble in alcohol and water but cannot be successfully recrystallized from these solvents as the substance obtained on evaporating the solvents sets to a hard mass on drying. It decomposes with a flash and a large amount of smoke when a flame is applied to it or when touched with concentrated sulfuric acid, leaving a black residue behind.

Tetramethylammonium Chlorate, $N(CH_3)_4ClO_3$.—This is prepared by the double decomposition between tetramethylammonium iodide and silver chlorate and evaporating the resulting solution on the water bath to crystallization. As thus obtained, it consists of white crystals. It is freely soluble in alcohol and water. It explodes at 230° . It takes fire suddenly on presenting to a flame or touching with a drop of concentrated sulfuric acid.

0.0659 g. gave 5.25 cc. N_2 at 23° and 765 mm.; N, 9.02.
Calc. for $N(CH_3)_4ClO_3$: N, 8.89.

Tetraethylammonium Chlorate, $N(C_2H_5)_4ClO_3$.—This has been similarly prepared by the double decomposition between tetramethylammonium iodide and silver chlorate and evaporating the resulting solution on the water bath to crystallization when crystals are obtained on cooling. As thus obtained, the substance is quite pure. It can be recrystallized from water or alcohol. It melts with decomposition at 223° . It takes fire as usual when a flame is applied to it or when it is touched with a drop of concentrated sulfuric acid.

0.0895 g. gave 5 cc. N_2 at 24° and 766 mm.; N, 6.4.
Calc. for $N(C_2H_5)_4ClO_3$: N, 6.56.

Tetrapropylammonium Chlorate, $N(C_3H_7)_4ClO_3$.—This has been obtained as usual by the double decomposition between silver chlorate

and tetrapropylammonium iodide and evaporating the resulting solution on the water bath to crystallization. The chlorate melts at 217° without decomposition. It dissolves freely in water and alcohol. It burns off as usual on the presentation of a flame or when touched with concentrated sulfuric acid.

0.1444 g. gave 3.9 cc. N_2 at 25° and 767 mm.; N, 5.52.

Calc. for $N(C_2H_5)_4ClO_3$: N, 5.2.

Dimethylphenylbenzylammonium Chlorate, $N(CH_3)_2(C_6H_5)C_7H_7ClO_3$.

—This salt is prepared from dimethylphenylbenzylammonium bromide and silver chlorate by double decomposition and evaporating the solution in a vacuum over sulfuric acid. The chlorate obtained is white and crystalline in shape. It is hygroscopic and dissolves freely in water and alcohol. It decomposes without any sharp explosion at 137° , leaving a red mass as residue which does not melt on further heating. It, however, burns with a flash and decomposes explosively with concentrated sulfuric acid, and slowly decomposes to a gray mass on leaving it at the ordinary temperature for several days.

0.1527 g. gave 6.75 cc. N_2 at 24° and 763 mm.; N, 5.0.

Calc. for $N(CH_3)_2(C_6H_5)(C_7H_7)ClO_3$: N, 4.74.

Diethylphenylbenzylammonium Chlorate, $N(C_2H_5)_2C_6H_5C_7H_7ClO_3$.—

This is prepared as usual by the double decomposition between the corresponding chloride and silver chlorate and evaporating the resulting solution in a vacuum over sulfuric acid. This is obtained in white crystals melting to a dark liquid at 77° . On further heating it becomes darker and darker until at 125° it decomposes with effervescence. It decomposes partly on leaving it for long periods in the air. It is soluble in water and alcohol and burns with a flash.

0.1623 g. gave 6.1 cc. N_2 at 765 mm.; N, 4.24.

Calc. for $N(C_2H_5)_2C_6H_5C_7H_7ClO_3$: N, 4.33.

Trimethylsulfine Chlorate, $S(CH_3)_3ClO_3$.—This salt is obtained by the double decomposition between silver chlorate and trimethylsulfine iodide and evaporating the resulting solution on the water bath. The salt could be recrystallized from water with difficulty since this salt is very soluble in cold water and the difference in solubility in hot and cold water is very small. It explodes at 170° . The salt explodes sharply on presenting a flame to it, the explosion being very rapid and sharp. It is hygroscopic and liquefies when exposed to air.

0.1474 g. gave 0.1212 CO_2 and 0.0666 g. H_2O ; C, 22.32; H, 5.91.

Calc. for $S(CH_3)_3ClO_3$: C, 22.44; H, 5.61.

Oxidation of Organic Iodo-Compounds by Means of Chloric Acid.

Iodoxy-benzene, $C_6H_5IO_2$.—A little iodobenzene is taken in a crystallizing dish and to it is added an excess of concentrated chloric acid solu-

tion and kept aside for about two days. In the course of this period slightly yellow crystals appear. On washing with alcohol, in which it is insoluble, it is obtained in clear, white crystals. The substance explodes at $227-228^{\circ}$. An iodine estimation gave the following results:

0.1251 g. gave 0.1251 AgI; I, 54.03. Calc. for $C_6H_4IO_2$: I, 53.81.

***o*-Iodoxy-toluene**, $CH_3.C_6H_4IO_2$.—This is obtained similarly to the above substance by allowing *o*-iodotoluene to remain in contact with chloric acid for several days. A crystalline product is obtained which is thoroughly washed with alcohol and separated by filtration. The product decomposes at 210° .

0.0855 g. gave 0.0854 AgI; I, 51.04. Calc. for $CH_3.C_6H_4IO_2$: I, 50.8.

***p*-Iodoxy-toluene**, $CH_3.C_6H_4IO_2$.—This is obtained by exactly the same procedure as the previous compound. *p*-Iodotoluene is left for several days in contact with concentrated chloric acid. The crude product thus obtained is washed with alcohol. It decomposes at 229° .

0.1213 g. gave 0.1133 AgI; I, 50.73. Calc. for $CH_3.C_6H_4IO_2$: I, 50.8.

Iodoxy-*m*-xylene, $C_6H_3(CH_3)_2(IO_2)^4$.—This is obtained by keeping the iodocompound with a strong solution of chloric acid for two or three days at ordinary temperature. The resulting product is thoroughly washed with alcohol and is found to be iodoxy-*m*-xylene, exploding at 193° .

0.0709 g. gave 0.0627 g. AgI; I = 47.12. Calc. for $C_6H_3(CH_3)_2(IO_2)_4$: I = 48.11.

Iodoxy-*o*-xylene, $C_6H_3(CH_3)_2(IO_2)^4$.—This compound has been prepared for the first time, since it was not known before. Yellowish crystals were obtained by treating iodo-*o*-xylene with concentrated chloric acid in the cold for several days. On washing with alcohol the substance is obtained pure. It explodes at $192-193^{\circ}$. The salt was analyzed with the following result:

0.0989 g. gave 0.1310 CO_2 and 0.0817 g. gave 0.0729 g. AgI.

Calc. for $C_6H_3(CH_3)_2(IO_2)_4$: C, 36.36; H, 3.41; I, 48.11. Found: C, 36.18; H, 3.58; I, 48.9.

Iodoxy-mesitylene, $C_6H_2(CH_3)_3IO_2$.—This substance is obtained by keeping iodomesitylene for a few days in contact with strong chloric acid. The crystalline crude product thus obtained is washed with alcohol. It decomposes at 194° .

0.1415 g. gave 0.1191 g. AgI; I, 45.53. Calc. for $C_6H_2(CH_3)_3IO_2$: I, 45.68.

Investigations on similar lines are being continued.

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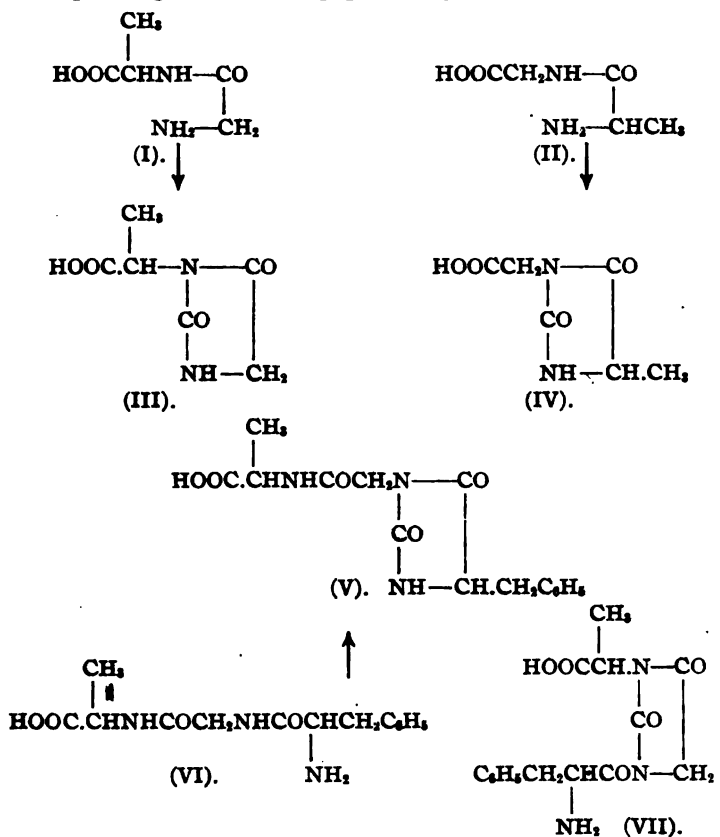
[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON HYDANTOINS. XXXVII. SYNTHESIS OF THE POLYPEPTIDE-HYDANTOIN—PHENYLALANYL-GLYCINE-HYDANTOIN.¹

BY TREAT B. JOHNSON AND JOSEPH S. BATES.

Received March 14, 1916.

A *polypeptide-hydantoin*, as we shall apply the term in our work, is a cyclic derivative of a polypeptide containing a hydantoin ring, which has been incorporated by joining together two nitrogen atoms of the peptide with CO in the form of a urea, and in which the characteristic grouping of the polypeptide has been preserved. For example, the hydantoins represented by Formulas III and IV are two representatives of this type of compounds and are the only hydantoins that can be constructed from their corresponding isomeric dipeptides—glycylalanine I, and alanyl-

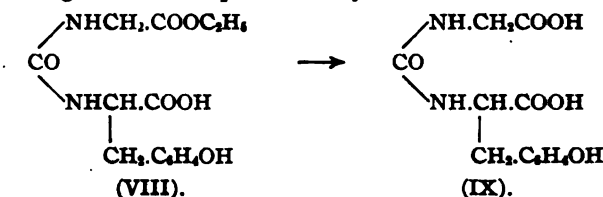


¹ Part of a dissertation presented by Mr. Joseph Sumner Bates to the Faculty of the Graduate School of Yale University, 1915, in candidacy for the Degree of Doctor of Philosophy.

glycine II. In other words, a polypeptide-hydantoin is a cyclic combination of a peptide which does not contain an unsubstituted, diacid-amide grouping —CO.NH.CO— and therefore cannot break down on hydrolysis with evolution of ammonia. In the case of the higher polypeptides the possibilities of forming cyclic combinations are much greater. For example, it is possible, theoretically, to derive from the tripeptide-phenylalanylglycylalanine VI, two isomeric polypeptide-hydantoins corresponding to Formulas V and VII.

Combinations of these types have never been prepared and, as we have indicated in a preliminary paper,¹ a knowledge of their properties is very desirable from a biochemical standpoint. The writer also anticipates that an investigation of certain combinations, which may be derived from the hydantoins III and IV, will be productive of results from which more definite conclusions may be drawn regarding the tautomeric behavior of the hydantoin ring.

Symmetrically substituted ureas of α -aminoacids have been described by Morel² and were prepared by the action of the isocyanate- $\text{OCN.CH}_2\text{COOC}_2\text{H}_5$ —on α -aminoacids in the presence of dilute alkali. He prepared in this manner from tyrosine the urea represented by Formula VIII. This was not isolated but was converted by hydrolysis with alkali into its corresponding acid urea represented by Formula IX. He also applied a



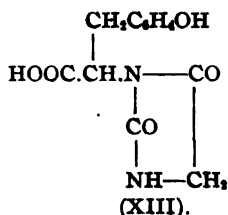
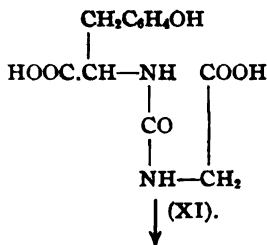
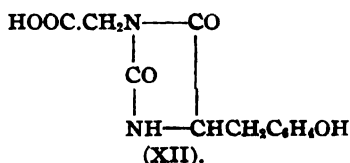
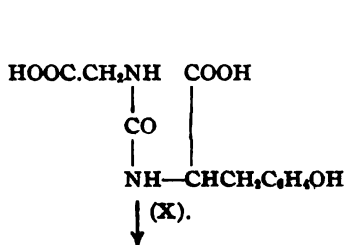
similar reaction with leucine. Combinations corresponding to Formula IX are closely related to the compounds under discussion in this paper, being derivatives of hydantoic acid, and theoretically should condense to *polypeptide-hydantoins* by the action of mineral acids. Morel,³ however, did not consider apparently the possibility of accomplishing such condensations, perhaps because he recognized the impossibility of establishing the constitution of the resulting hydantoin from that of its precursor—the urea. For example, the urea IX, may be viewed either as a N-derivative of the hydantoic acid of tyrosine or of plain hydantoic acid as represented by Formulas X and XI, respectively. By digestion of such a compound with acids, therefore, either one of the two carboxyl groups might be involved in the condensation, leading theoretically to the

¹ Johnson, *Proc. Nat. Acad. Sci.*, 2, 69 (1916); *Chem. News*, 113, 127 (1916) (Paper XXXVI).

² *Compt. rend.*, 143, 119 (1906).

³ *Loc. cit.*

formation of two isomeric polypeptide-hydantoin as represented by Formulas XII and XIII, respectively. It would be a difficult matter to decide which isomer was formed here, unless some method of synthesis was available whereby the two compounds could be prepared in another manner. In this paper, we shall now describe methods of synthesizing such cyclic combinations and give a description of the synthesis and properties of the cyclic peptide—*phenylalanylglycine-hydantoin* (XXIII).



That N-substituted hydantoin may be prepared by interaction of the alkali or silver salts of hydantoin with halides has been known for a long time and the experimental data, so far obtained, leads to the conclusion that the structure of the products formed depends upon the saturation of the grouping occupying the 4-position of the hydantoin ring. In the case of plain hydantoin and related, saturated methylene derivatives, so far examined, the 1-position of the ring is the point of attack and the formation of 3- and 1,3-alkyl derivatives has never been observed.¹ In order to render both nitrogen atoms of the hydantoin susceptible to attack under the above conditions, it is apparently necessary to destroy the influence of the methylene combination in position 4 and increase the negative character of the ring by incorporation of an unsaturated grouping in this position. In such cases dialkyl-compounds can be obtained by alkylation, but it still holds here also that the 1-position of the ring is the first point of attack and that isomeric 3-alkyl hydantoin have never been isolated.²

¹ Franchimont and Klobbie, *Rec. trav. chim.*, 8, 283 (1889); Harries and Weiss, *Ann.*, 327, 355 (1902); Harries, *Ibid.*, 361, 69 (1908); Siemonsen, *Ibid.*, 333, 101 (1904); Neubauer, *Ibid.*, 137, 288 (1866); Biltz, *Ber.*, 41, 1379 (1908); Weitzner, *Ann.*, 362, 125 (1908).

² Johnson and Nicolet, *THIS JOURNAL*, 34, 1048 (1912); *Am. Chem. J.*, 47, 459 (1912); Johnson and Bengis, *THIS JOURNAL*, 35, 1606 (1913).

The starting point of the work to be described in this paper was 4-benzalhydantoin (XIV), which was prepared according to the method described by Wheeler and Hoffmann¹ namely, by condensing benzaldehyde with hydantoin. The *cis*-modification of the hydantoin² was the form used in our investigation. We now find that the sodium salt of this hydantoin interacts with ethyl chloroacetate in alcohol solution with substitution in position 1 forming chiefly the ester represented by Formula XVII. There is also formed at the same time a very small amount of an isomeric product which we have represented as a stereoisomeric modification of the hydantoin as represented by Formula XVIII. We were unable to establish definitely its constitution on account of our inability to obtain it in sufficient quantity for experimental purposes. The unsaturated hydantoin (XVII) is easily reduced at the double bond by the action of stannous chloride in hydrochloric acid and also by zinc in acetic acid giving the saturated ester—ethyl 4-benzylhydantoin-1-acetate (XXI). Hydrolysis of the ester (XXI) with hydrobromic acid leads smoothly to the formation of the unsaturated acid (XX). We succeeded in identifying only one modification of this hydantoin. Its potassium salt is easily obtained by digestion of the ester (XXI) with an alcoholic solution of potassium hydroxide. When the acid (XX) was reduced by treatment with tin and hydrochloric acid it was converted into the corresponding 4-benzylhydantoin-1-acetic acid or *phenylalanylglycine-hydantoin* represented by Formula XXIII.

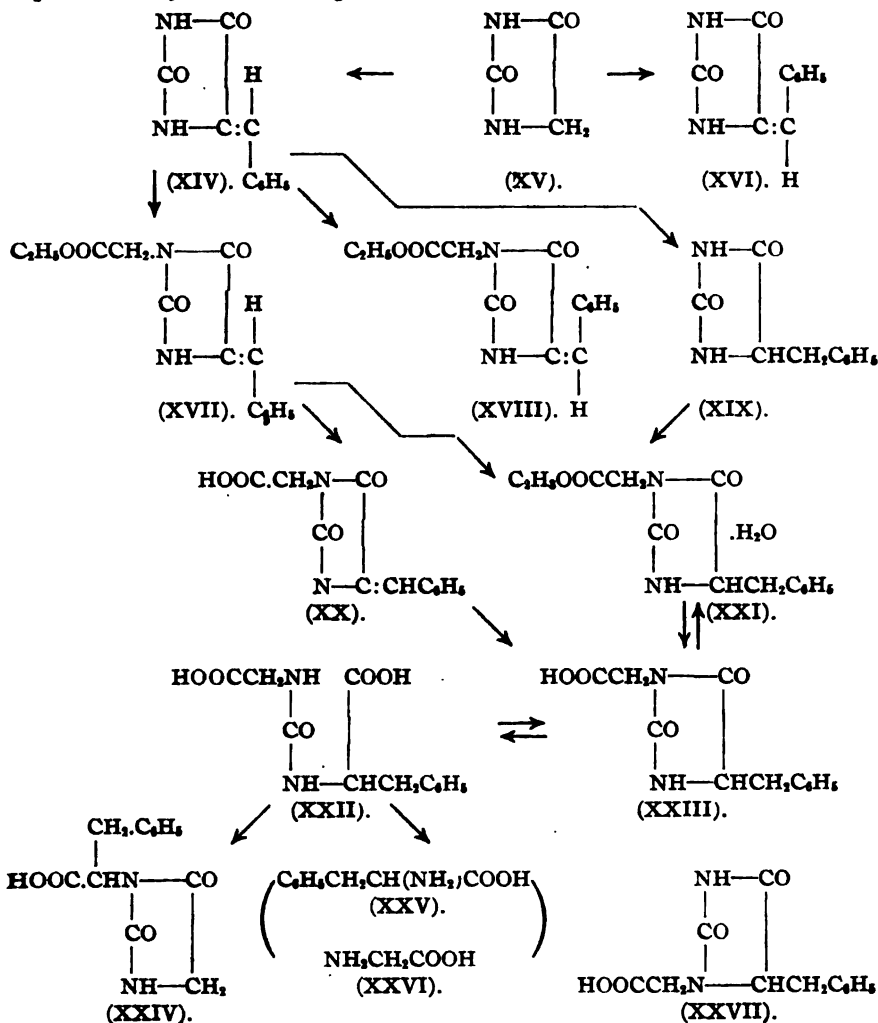
4-Benzylhydantoin-1-acetic acid (XXIII), on esterification with alcohol, is transformed smoothly into the ester (XXI), which undergoes hydrolysis by digestion with hydrochloric and hydrobromic acids, giving again the polypeptide-hydantoin (XXIII). The same saturated ester (XXI) described above is also obtained in excellent yield by alkylation of 4-benzylhydantoin (XIX) with ethyl chloroacetate. Therefore the same ester (XXI) is obtained from 4-benzalhydantoin (XIV) whether one first alkylates with ethyl chloroacetate and then reduces the double bond of the resulting hydantoin (XVIII), or first reduces to 4-benzylhydantoin and finally alkylates with the halogenated ester $\text{ClCH}_2\text{COOC}_2\text{H}_5$.

The hydantoin ring of the polypeptide-hydantoin (XXIII) is easily hydrolyzed by digestion of the hydantoin with an excess of potassium hydroxide forming the dipotassium salt of the acid (XXII). When this is heated above its melting point, water is given off and it is transformed into the original hydantoin (XXIII) melting at 184° . The same change is accomplished by digesting the acid (XXII) with hydrochloric acid. In other words, the carboxyl of the glycine group is not involved in this inner condensation leading to the formation of the isomeric polypeptide-

¹ *Am. Chem. J.*, 43, 368 (1910).

² Johnson and Bates, *THIS JOURNAL*, 37, 383 (1915).

hydantoin (XXIV). Complete hydrolysis of the polypeptide-hydantoin (XXIII) is easily accomplished by heating with hydrochloric acid at 140° . It breaks down completely under these conditions with formation of phenylalanine (XXV), glycocoll (XXVI) and carbon dioxide. We obtained no evidence of the formation of ammonium chloride by this treatment, proving thereby that the acetic acid group was substituted in the 1-position of the hydantoin ring. The isomeric hydantoin represented by Formula XXVII would break down on hydrolysis with formation of ammonia, carbon dioxide and the imino acid— $\text{HOOC} \cdot \text{CH}_2 \cdot \text{NHCH} \cdot (\text{COOH}) \text{CH}_2 \text{C}_6\text{H}_5$. The various transformations described above are represented by the following formulas:



Experimental Part.

All the hydantoin employed in this investigation was prepared according to the directions of Siemonsen.¹

4-Benzalhydantoin, $\text{CO.NH.CO.NH.C} : \text{CHC}_6\text{H}_5$.—This was prepared

by condensation of hydantoin with benzaldehyde as described by Wheeler and Hoffmann.²

3-Acetyl-4-benzalhydantoin, $\text{CO.NH.CO.N(COCH}_3\text{).C} : \text{CHC}_6\text{H}_5$.—This

new hydantoin is easily prepared by the action of acetic anhydride on benzalhydantoin. Two grams of the hydantoin were dissolved in the anhydride and the solution heated in an oil bath at $155\text{--}165^\circ$ for 4 hours. On cooling the solution this acetyl derivative separated. It was purified by crystallization from glacial acetic acid and deposited in the form of colorless, transparent plates melting at 223° to a red oil with slight effervescence. A mixture of this compound with 4-benzalhydantoin melted at $197\text{--}198^\circ$.

Calc. for $\text{C}_{12}\text{H}_{10}\text{O}_2\text{N}_2$: N, 12.16. Found: N, 12.14, 12.01.

Ethyl *cis*-4-Benzalhydantoin-1-acetate (XVIII).—This is the chief product of the reaction when the sodium salt of 4-benzalhydantoin interacts with ethyl chloroacetate in ethyl alcohol. To prepare the hydantoin 10 g. of the benzal derivative were suspended in a solution of 1.3 g. of sodium in 100 cc. of absolute alcohol. This mixture was then heated to boiling until the hydantoin was completely transformed into its sodium salt, which separated as a colorless powder insoluble in the alcohol. Seven grams of ethyl chloroacetate and a molecular proportion of potassium iodide were then added and the digestion continued, by heating on the steam bath, until the alcohol gave a neutral reaction towards moist litmus and turmeric paper. The solution was then cooled and the insoluble material separated by filtration. Practically all the above hydantoin separated here with the inorganic salts. By trituration with cold water, it was obtained in a crystalline condition and was finally purified by crystallization from hot alcohol. It separated from this solvent in the form of rhombic prisms which melted at 174° to a clear oil without apparent decomposition. The yield of purified material was 8.5 g. or 60% of the theoretical quantity.

Calc. for $\text{C}_{14}\text{H}_{14}\text{O}_2\text{N}_2$: N, 10.21. Found: N, 10.12, 10.15.

In a second alkylation experiment the following proportions were used: 12.5 g. of the benzalhydantoin, 1.7 g. of sodium dissolved in 100 cc. of absolute alcohol, 8.3 g. of ethyl chloroacetate and 12.5 g. of potassium iodide. After digestion on the steam bath until the reaction was complete

¹ *Ann.*, 333, 101 (1904).

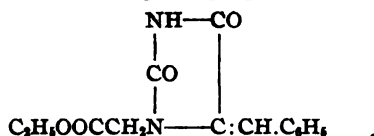
² *Loc. cit.*

the solution was cooled and the hydantoin-acetate filtered off with inorganic salts. This material was then washed with a small volume of cold water and finally dissolved in boiling alcohol to purify the hydantoin. The latter dissolved easily and separated, on cooling, in the form of plates melting at 174° . There was a small amount of material, however, which would not dissolve in the alcohol. This contained inorganic material and dissolved immediately in hot water. On acidifying this solution there was an immediate precipitate of a crystalline substance, which proved to be *4-benzalhydantoin-1-acetic acid* (see below). This crystallized from boiling alcohol in the form of rhombic prisms or tables which melted at $257-258^{\circ}$ to a clear oil.

The alcohol filtrates from experiment one (above) were concentrated and cooled when more of the hydantoin-acetate (m. 174°) was obtained together with a secondary product which melted several degrees lower. The latter was very soluble in alcohol and separated as needles which melted at 158° to a clear oil. The experimental evidence so far obtained points to the conclusion that this substance is a stereoisomeric modification of *ethyl 4-benzalhydantoin-1-acetate* (*trans* form). When boiled with strong potassium hydroxide solution no ammonia was evolved. We did not obtain enough of the compound to reduce it to the corresponding 4-benzylhydantoin.

Calc. for $C_{14}H_{14}O_3N_2$: N, 10.21. Found: N, 10.10.

The corresponding structural isomer *ethyl 4-benzalhydantoin-3-acetate* has never been described. An attempt to prepare this substance by condensa-



tion of ethyl hydantoin-3-acetate¹ $\text{C}_2\text{H}_5\text{OOC.CH}_2.\text{N}-\text{CO.NH.CO.CH}_2$

with benzaldehyde, in acetic acid and in the presence of anhydrous sodium acetate, was unsuccessful. This result is in accord with previous observations on the inactivity of 3-substituted hydantoins towards aldehydes.

4-Benzalhydantoin-1-acetic Acid, $\text{CO.N}(\text{CH}_2\text{COOH}).\text{CO.NH}-\text{C}:\text{CH}-$

C_6H_5 .—This acid is easily obtained by saponification of the above ester with acids and alkalis. Ten grams of the ester were digested with 75 cc. of hydrobromic acid for about 5 hours. The hydantoin remained insoluble throughout the operation and ethyl bromide was evolved. After removal of the excess of hydrobromic acid by evaporation at 100° , the acetic acid derivative was then washed with cold water, in which it is

¹ This hydantoin was kindly sent to me by Professor J. R. Bailey of the University of Texas (see *THIS JOURNAL*, 37, 935 (1915)).

practically insoluble, and purified by crystallization from hot alcohol. It separated from this solvent, on cooling, in the form of diamond shaped prisms which melted at 258° to a clear oil. From 10 g. of the ester were obtained 7.5 g. of the purified acid or 84% of a theoretical yield. The same acid was also obtained in the form of its potassium salt by saponifying the above ester with potassium hydroxide. Two grams of the ester and 0.4 g. of potassium hydroxide were digested with 50 cc. of 95% alcohol at 100° for one hour. The reaction was apparently complete at the end of this time and the potassium salt of the acid had separated as colorless prisms. These were separated and dissolved in water. On acidifying the aqueous solution with hydrochloric acid the hydantoin separated at once and melted at $256-258^{\circ}$.

Calc. for $C_{12}H_{10}O_4N_2$: N, 11.38. Found: N, 11.36, 11.30.

4-Benzylhydantoin, $CO.NH.CO.NH.CH_2CH_2C_6H_5$.—Wheeler and Hoff-

mann¹ prepared this compound by reduction of 4-benzalhydantoin with hydriodic acid and phosphorus, and also with aluminum amalgam in alkaline solution. Wheeler, Hoffmann and Johnson² showed that the same change can be effected by digesting the benzal derivative with tin and hydrochloric acid but obtained a poor yield of the reduced hydantoin. By slight changes in procedure we find that the reduction can be accomplished quantitatively by means of these reagents. Ten grams of the 4-benzalhydantoin were digested, on a sand bath, with 20 g. of mossy tin and 300 cc. of 20% hydrochloric acid. When complete reduction had taken place the hydantoin had completely dissolved giving practically a colorless solution. The solution was filtered and the excess of hydrochloric acid removed by evaporation at 100° . The residue of tin chloride and reduced hydantoin was then dissolved in hot water and the tin precipitated by addition of an excess of aqueous ammonia. The precipitate of stannous hydroxide was filtered off and the filtrate, after acidifying with hydrochloric acid, evaporated to dryness. The residue left behind was then triturated with cold water to remove ammonium chloride when the benzyhydantoin remained undissolved. This was purified by crystallization from hot alcohol and separated, on cooling, in the form of colorless prisms melting at 190° to a clear oil. From 10 g. of the unsaturated hydantoin we obtained 9 g. of this purified benzalhydantoin or 90% of a theoretical yield.

This same hydantoin can also be prepared by reduction of 4-benzalhydantoin with zinc and acetic acid. Two grams of the benzal derivative were dissolved in 40 cc. of hot, glacial acetic acid and 5 g. of powdered zinc added to the solution. The mixture was then boiled for several hours

¹ *Am. Chem. J.*, **45**, 372 (1911).

² *J. Biol. Chem.*, **10**, 147 (1911).

and the solution evaporated to dryness after filtering off undissolved zinc. The residue obtained was then triturated with 10 cc. of water acidified with hydrochloric acid to remove zinc and the insoluble hydantoin separated. It was purified by crystallization from alcohol and melted at 190° . We obtained 1.8 g. of benzylhydantoin corresponding to a yield of 90% of the theoretical.

4-Benzylhydantoin-1-acetic Acid, $\text{CO.N}(\text{CH}_2\text{COOH})\text{CONH.CH.CH}_3$.

C_8H_8 .—This acid is easily prepared by reduction of the corresponding benzal derivative with tin and hydrochloric acid. Five grams of the benzal derivative and 10 g. of mossy tin were digested with 150 cc. of 20% hydrochloric acid. At the end of 4 hours the hydantoin had completely dissolved indicating complete reduction. After filtering, the acid solution was evaporated to dryness and the tin removed by precipitation with ammonia. On evaporating the ammoniacal filtrate and finally triturating the residue obtained with cold water the above acid remained undissolved. It was purified by recrystallization from boiling water and separated, on cooling, as flat, colorless prisms or rhombic plates, which melted at 184 – 185° to a clear oil without effervescence.

Calc. for $\text{C}_8\text{H}_8\text{O}_4\text{N}_2$: N, 11.29. Found: N, 11.02.

This same acid was also prepared from ethyl 4-benzylhydantoin-1-acetate (see below) by saponification with hydrobromic and hydrochloric acid. The simplest means of accomplishing the change was found to be the evaporation in an open dish, of a solution of the ester in a considerable excess of 25–30% hydrochloric acid. The ester dissolved almost immediately in the acid on boiling. After evaporation, the residue consisted of pure 4-benzylhydantoin-1-acetic acid melting at 184° to a clear oil. From 9.7 g. of the ester we obtained 7.8 g. of the purified acid.

Calc. for $\text{C}_{12}\text{H}_{12}\text{O}_4\text{N}_2$: N, 11.29. Found: N, 11.10, 11.18.

Ethyl 4-Benzylhydantoin-1-acetate, $\text{C}_8\text{H}_8\text{OOCCH}_2\text{—N—CO—CH}(\text{CH}_2\text{C}_6\text{H}_5)\text{.NH—CO.H}_2\text{O}$.—This ester is easily obtained by

alkylation of 4-benzylhydantoin, in alcohol solution and in the presence of sodium ethylate, with ethyl chloroacetate. After the reaction was complete, the alcohol was removed by evaporation and the residue triturated with cold water to remove sodium chloride. The undissolved hydantoin was then purified by crystallization from boiling water. It separated from this solvent, on cooling, as beautiful, colorless needles, which melted at 157° to a clear oil. The hydantoin is soluble in alcohol. From 10 g. of 4-benzylhydantoin we obtained 11.6 g. of the purified ester. This same hydantoin is also formed by esterification of the corresponding acid (see above). Two grams of the acid and 2 cc. of concentrated sulfuric acid were dissolved in 25 cc. of absolute alcohol and the mixture

boiled for 5 hours. The excess of alcohol was then removed by evaporation at 100° and the resulting ester purified by recrystallization from alcohol. It melted at 157° .

Ethyl 4-benzylhydantoin-1-acetate was also prepared by a third method, namely, by reduction of ethyl 4-benzalhydantoin-1-acetate with zinc and acetic acid. Three grams of the unsaturated ester were dissolved in 50 cc. of hot glacial acetic acid and 5 g. of powdered zinc suspended in the solution. After boiling the solution for 25 to 30 hours (using return condenser) the undissolved zinc was removed by filtration and the solution finally evaporated to dryness. The crystalline residue obtained was triturated with 10 cc. of cold dilute hydrochloric acid to remove any zinc and the hydantoin purified by crystallization from alcohol. It separated in the form of needles and melted at $155-156^{\circ}$.

We also prepared this ester by reducing ethyl 4-benzalhydantoin-1-acetate with stannous chloride. Eight grams of the unsaturated hydantoin and 10-12 g. of stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) were dissolved in 200 cc. of 95% alcohol and the solution saturated hot with hydrochloric acid gas. After reducing in the acid solution for 8-10 hours the alcohol was then evaporated and the residue obtained triturated with cold water to remove tin chloride. The hydantoin-acetate remains behind undissolved and was purified by crystallization from boiling alcohol. It melted at 157° to a clear oil. Repeated nitrogen determinations, both by the Kjeldahl and Dumas methods, consistently indicated that this ester crystallized with a molecule of water. The compound did not lose weight when heated at 100° .

Calc. for $\text{C}_{14}\text{H}_{16}\text{O}_4\text{N}_2 \cdot \text{H}_2\text{O}$: N, 9.52. Found: N, 9.52, 9.53, 9.55, 9.60, 9.48.

Sym-Phenylalanine-glycine Urea, (XXII).—This acid was obtained in the form of its dipotassium salt by saponification of the ethyl 4-benzylhydantoin-1-acetate with potassium hydroxide. Three grams of the ester and 2 g. of potassium hydroxide (3 molecular proportions) were dissolved in 50 cc. of water and the solution heated on a steam bath for 5 hours. Dilute hydrochloric acid was then cautiously added until the mixture was neutral to turmeric and litmus and the solution finally evaporated nearly to dryness. This concentrated solution was then desiccated in a vacuum over concentrated sulfuric acid. The crystalline residue obtained was then triturated with cold alcohol when the potassium salt of the urea acid dissolved and could be separated easily from potassium chloride. On concentrating the alcoholic solution and cooling the potassium salt of the above acid finally deposited in the form of colorless needles. They decomposed when heated at $268-269^{\circ}$.

Calc. for $\text{C}_{15}\text{H}_{15}\text{O}_4\text{N}_2\text{K}_2$: K, 22.87. Found: K, 22.40.

In order to obtain the free acid the dipotassium salt was suspended in 25 cc. of dry benzene and dry hydrochloric acid gas passed into the

mixture at room temperature for 2 hours. Neither the salt nor the corresponding acid was soluble in this solvent. The benzene was finally allowed to evaporate spontaneously and the potassium chloride, formed during the reaction, dissolved by trituration with cold water. The urea-acid was not dissolved by this solvent (cold) but was soluble in hot water and crystallized on cooling in colorless, elongated prisms which melted at $176-177^{\circ}$ with violent effervescence. When this acid was melted and the resulting oil was cooled it solidified again. On reheating this product it was not changed at $176-7^{\circ}$, but melted sharply at 184° to a clear oil. In other words, the acid loses water at the temperature of its melting point and is converted into 4-benzylhydantoin-1-acetic acid (m. 184°) or (phenylalanine-glycine hydantoin).

Calc. for $C_{12}H_{14}O_4N_2$: N, 10.39. Found: N, 10.36.

Hydrolysis of Ethyl 4-Benzylhydantoin-1-acetate with Hydrochloric Acid.—One gram of the hydantoin and 15 cc. of concentrated hydrochloric acid were heated in a pressure tube at $140-146^{\circ}$ for 3.5 hours. When the tube was opened there was slight pressure, due to the presence of carbon dioxide, and a crystalline product was suspended in the acid solution. This material was extremely soluble in cold water and was apparently a mixture of the hydrochlorides of glycol and phenylalanine. This material was separated by filtration and examined as follows: A portion of the material was dissolved in water and the solution made strongly alkaline by addition of sodium hydroxide. On boiling this solution there was no evolution of ammonia. The original acid filtrate likewise gave no ammonia when digested with an excess of alkali. The remainder of the material was then repeatedly recrystallized from dilute hydrochloric acid when a definite crystalline product was easily obtained which deposited in the form of rosetts of prisms. The substance contained chlorine and decomposed with effervescence when heated above 235° . It was dried at $90-100^{\circ}$. A nitrogen determination indicated that we were dealing with the hydrochloride of phenylalanine originally described by Erlenmeyer and Kunlin.¹

Calc. for $(C_9H_{11}O_2N)_2HCl$: N, 7.69. Found: N, 7.9.

Hydrolysis with an Aqueous Solution of Potassium Hydroxide.—Fifteen-tenths of a gram of ethyl 4-benzylhydantoin-1-acetate and 1.0 g. of potassium hydroxide were dissolved in 10 cc. of water and the solution boiled for one-half hour in order to obtain the dipotassium salt of *sym*-phenylalanine-glycine urea. There was no evolution of ammonia during this operation. The aqueous solution was then evaporated to dryness at 100° and the residue dissolved in an excess of dilute hydrochloric acid and the solution evaporated again. The crystalline residue obtained here was then triturated with cold water to remove potassium chloride

¹ *Ann.*, 307, 160 (1899).

and the crystalline product left behind purified by recrystallization from boiling water. It separated, on cooling, in the form of prismatic crystals which melted at 183–184° to an oil. A mixture of this with *phenylalanylglycine-hydantoin* (m. 184°) melted at the same temperature.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT KANSAS AGRICULTURAL EXPERIMENT STATION.]

A STUDY OF CERTAIN CONDITIONS WHICH AFFECT THE ACTIVITY OF PROTEOLYTIC ENZYMES IN WHEAT FLOUR.

BY C. O. SWANSON AND E. L. TAGUE.

Received February 16, 1916.

Introduction.

A study on conditions which affect the activity of amylolytic enzymes in wheat flour was reported in a previous paper.¹ In that study several facts were noticed which deserve further investigation. In planning for such work it was seen that the proteins of the flour were involved, and therefore it was thought best first to make a study of certain conditions which affect the activity of proteolytic enzymes of wheat flour.

In this investigation we used a high-grade patent flour, made by the Department of Milling Industry. Such a flour is desirable because it consists mostly of the pure floury endosperm of the wheat kernel, and has a low ash content.

The proteins of wheat flour have been the object of a large amount of investigation. Osborne and Voorhees² separated the nitrogenous substances in wheat flour into five distinct proteins known as gliadin, glutenin, globulin, leucosin, and proteose. Because of the number and complex nature of the proteins of wheat flour it was decided to confine this study to the protein leucosin freely soluble in pure water.

It is recognized that the figures obtained would have been different had we used the whole ground wheat kernel, or flour less free from proteins of the bran coat and germ. The results would probably also have been different had the other proteins of the flour been included. It is planned to continue this experiment under conditions where the other proteins of the flour are included, and also on the whole ground wheat kernel.

Methods of Experimentation.

A large number of preliminary trials were made in order to determine the best methods of procedure. In this report are presented only the results of trials that were found workable and of value in this study. The data obtained in the different trials are not given in the chronological order of performance, but in a manner calculated to make the report clear.

¹ THIS JOURNAL, 35, 1635–1643 (1913).

² *Am. Chem. J.*, 15, 392–471 (1893).

All of the determinations were made in quadruplicate, and wherever the agreement was not within reasonable limits, the trial was repeated. The results here given are the average of the determinations made under acceptable conditions.

The general plan of procedure was to digest a water extract of flour under the conditions of the trial and then determine the increase in the content of nitrogen in the amino form. For determining the amount of nitrogen in this form at any stage of the experiment, the formal titration as elaborated by Sørensen¹ was employed. By using the water extract, the study is confined principally to the action of proteolytic enzymes on the water-soluble protein known as leucosin. The acids, alkali, salts, or other substances used in this study were added to the flour extract.

The water extract from sound flour contains nitrogenous compounds having free amino and carboxyl groups. If this extract is neutralized and then formaldehyde added, the amount of titrable material is always a measurable quantity. It is necessary to determine the amount of such titrable material before we can measure the protein cleavage due to the action of proteolytic enzymes. This determination is reported as the blank in the tables that follow.

In this investigation the influence of bacterial action was eliminated by the use of neutral toluene water in making the extractions and digestions. Ordinary distilled water was made neutral by passing through it air freed from carbon dioxide. To such water was added 5 cc. of neutral toluene for 8 liters, or a little more than $\frac{1}{2}$ cc. per liter. We believe that this amount of toluene was sufficient to inhibit bacterial action, because the extracts were always found neutral to litmus paper tested according to the method of Henriques and Sørensen,² and toluene was seen floating on the surface of the extract. If such an excess of toluene was not noticed more was added. In several preliminary trials four times the above amount of toluene was used, but the results were not essentially different from those obtained with the smaller quantity which was sufficient to provide an excess.

The following is a brief outline of the method we used in determining the amount of nitrogen in the amino form present in flour. For the sake of brevity, the nitrogen in amino form will be called the titrable nitrogen. A definite amount of flour is mixed with ten times its weight of neutral toluene water, and shaken at frequent intervals for one hour. This is then allowed to settle for 30 minutes. If the extraction is to be made at a given temperature it is necessary to heat the water and flour to this temperature before mixing and then keep the container in a thermostat for the re-

¹ H. Jessen-Hanse in "Handbuck der Arbeitsmethoden von Abderhalden, V," 6, 262-277.

² *Z. physiol. Chem.*, 64, 133; also "Handbuch der Arbeitsmethoden," *loc. cit.*

quired time. A narrow-mouth glass stoppered bottle is a convenient container. After settling, the supernatant liquid is filtered first through cotton, then through folded filter paper. Measure four 100 cc. portions into Erlenmeyer flasks, marked, say, *a*, *b*, *c*, *d*. Using these proportions of flour and water gives the results as titrable material in the extract from 10 g. of flour. To *c* and *d* add 5 cc. of solution of thymolphthalein, made by dissolving 0.5 g. in 1000 cc. of 93% neutral alcohol, and also 10 cc. of 40% formaldehyde neutral to the thymolphthalein solution, and let stand 15 minutes or more. While waiting, titrate flasks *a* and *b* with 0.05 *N* Ba(OH)₂, using 5 cc. of a 0.5% neutral alcoholic solution of phenolphthalein as indicator. The titration of flasks *a* and *b* is called the first stage. When solutions *c* and *d* have stood 15 minutes or more titrate to a faint blue. This end point is quite delicate and there is no difficulty in getting the exact reading. The titration of *c* and *d* is called the second stage. The average reading for *a* and *b* subtracted from the average reading for *c* and *d* gives the figure for calculating the amount of titrable nitrogen. If 0.05 *N* alkali is used the difference times 0.7 gives the milligrams titrable nitrogen in the extract.

As a check on the work, add the formaldehyde to flasks *a* and *b* as soon as the first stage titration is completed, and let stand 15 minutes or more. Titrate to a faint pink, then add the alkali, drop by drop, shaking well, till the rose-red color is obtained. It will be found that the total amount of alkali added to *a* and *b* is less than that added to *c* and *d* if the titration is stopped when the faint pink color is obtained in the second stage, but if the titration is continued to a rose-red the amounts will be practically equal. That it is necessary to titrate to a deep rose-red when phenolphthalein is used as indicator was determined by dissolving several pure amino acids in neutral water and then titrating, similar to what was done by Sørensen. If the titration is carried to a faint pink, only about 95% of the nitrogen in the amino form is obtained.

In making any formal titration, after ascertaining that the solution is neutral, it is necessary to make sure that no ammonia is present. It was found that all flour extracts used in this investigation, unless acids or alkali had been added, were neutral, and that no ammonia was present.

While flour extract is neutral to this litmus paper, it is not neutral to phenolphthalein, as shown by the titrable material obtained in the first stage. The neutralization of the alkali used in the first stage is due to the presence of acid phosphates, organic acids, if such are present, or any substance in the flour that has the power to neutralize an alkali. The substances in the flour extract which neutralize the alkali in the first stage have been discussed by Swanson in a previous paper.¹ This first stage is the usual method of determining acidity in wheat flour.

¹ *J. Ind. Eng. Chem.*, 4, 274 (1912); also *Kans. Agr. Expt. Sta., Bull.* 202.

Why is it necessary to titrate portions *a* and *b*? Why not titrate portions *c* and *d* in the two stages? Phenolphthalein is a more sensitive indicator for the first stage, and it is necessary first to measure as far as possible the neutralization due to substances other than the carboxyl groups which are a part of the amino acids, if we are to obtain a true measure of nitrogen in the amino form. That these substances neutralized in the first stage are mostly acid phosphates is probable from the work referred to above. Thymolphthalein is a more sensitive indicator for the second stage with opalescent solutions like these flour extracts. With phenolphthalein it is difficult to determine the amount of alkali to add beyond the faint pink end point to produce the required rose-red color. With clear solutions this difficulty is absent and the two stages of titration can be made on the same portion of extract, using phenolphthalein as indicator. The color end point for each stage is matched against a standard prepared each day, by adding to 100 cc. of neutral water 5 cc. of the phenolphthalein or thymolphthalein solution as the case may be, and exactly 8 drops of 0.05 *N* Ba(OH)₂.

Experimental.

The digestions were made at room temperature unless otherwise stated.

Trial I.—In order to determine the best proportion in which to mix flour and water, and the time necessary for complete extraction at 25°, flour and water were mixed in a bottle in the following proportions: 1 : 5, 1 : 10, 1 : 20, 1 : 50. These were shaken at frequent intervals, and at the end of definite periods small amounts were poured on four different folded filters, to get as rapid filtration as possible, and only enough was poured on the filter to give sufficient filtrate to measure portions large enough to represent the extract from 10 g. of flour. The main portion in the bottle was again shaken at frequent intervals, and at the end of the next period the filtration was repeated. The four portions obtained at the end of each period were titrated for the first and second stages, with the result given in cc. of Ba(OH)₂ neutralized.

TABLE I.—BEST PROPORTION IN WHICH TO MIX FLOUR AND WATER AND THE TIME NECESSARY FOR COMPLETE EXTRACTION AT 25°.

1:5.		1:10.		1:20.		1:50.		Time extracted.
1st.	2nd.	1st.	2nd.	1st.	2nd.	1st.	2nd.	
1.20	2.00	0.95	1.55	1.20	1.40	1.50	2.00	10 minutes
1.70	2.20	1.50	2.20	1.40	2.20	1.75	2.25	20 minutes
1.90	2.60	1.90	2.30	2.00	2.20	2.00	3.00	40 minutes
2.10	2.80	2.00	2.40	2.20	2.20	2.50	3.00	60 minutes
2.10	2.90	2.00	2.40	2.20	2.20	2.50	3.00	90 minutes
2.10	2.60	2.00	2.40	2.20	2.40	2.50	3.00	120 minutes

Proportion 1 : 5 was too concentrated and filtering was difficult. Proportion 1 : 50 was too dilute and the error on the end point relatively too large. Proportions 1 : 10 and 1 : 20 gave results that were practically the same.

Trial II.—This was a repetition of Trial I, except that the water was heated to 37° before it was mixed with the flour, and the bottle containing the mixture was kept at this temperature. The results show that more titrable material is extracted at 37° than at 25°, and also that the titrable material in the flour is extracted in an hour's time, and that extraction for another hour gives no important increase.

TABLE II.—BEST PROPORTION IN WHICH TO MIX FLOUR AND WATER AND THE TIME NECESSARY FOR COMPLETE EXTRACTION AT 37°.

1:5.		1:10.		1:20.		1:50.		Time extracted.
1st.	2nd.	1st.	2nd.	1st.	2nd.	1st.	2nd.	
1.80	2.00	2.00	2.20	2.40	1.60	2.00	3.00	10 minutes
2.00	2.40	2.30	2.70	2.40	2.40	2.25	3.75	20 minutes
2.10	2.70	2.55	2.70	2.40	2.40	2.50	4.00	40 minutes
2.40	2.70	2.60	2.70	2.60	2.40	2.50	4.00	60 minutes
2.20	3.00	2.60	2.70	2.60	2.40	2.50	4.00	90 minutes
2.30	3.00	2.60	2.70	2.60	2.60	2.50	4.00	120 minutes

Effect of Inorganic Compounds.

In the following tests it was necessary to have a large amount of flour extract. The extract for each test was prepared as follows: 700 g. of the flour were weighed into an 8-liter bottle. To this was added 7000 cc. of neutral toluene water, and the whole was shaken for one hour. It was then allowed to settle for one hour, and about 6000 cc. siphoned off and filtered, first through cotton and then through a folded filter. From this extract four 100 cc. portions were measured and titrated for the first and second stages. This constituted the blank titration. The rest of the flour extract was placed in a large bottle and used for the tests under the conditions given. Where the digestion was conducted at a temperature higher than that of the laboratory, a thermostat was used. This was provided with a stirrer and thermoregulator, and a constant temperature was easily maintained.

Trial III.—To determine the effect of digesting the flour extract alone. The flour extract was kept at a temperature of very nearly 40° and at the end of each week the amount of titrable material was determined. The amount of titrable material obtained in the first stage shows a slight increase during the first week, after which the results obtained are constant.

TABLE III.—RESULTS FROM DIGESTING THE FLOUR EXTRACT ALONE.

Time.	1st. stage.	2nd stage.	Milligrams N in amino form.
	Cc. 0.05 N Ba(OH) ₂ .	Cc. 0.05 N Ba(OH) ₂ .	
blank	3.3	2.7	1.89
1 week	4.3	3.6	2.52
2 weeks	4.1	4.4	3.08
3 weeks	4.4	4.9	3.43
4 weeks	4.4	6.0	4.20
5 weeks	4.4	6.0	4.20
6 weeks	4.2	6.4	4.48
7 weeks	4.3	6.2	4.34

The amount of titrable nitrogen obtained in the second stage increases slightly to the end of the fourth week, after which there is no definite change. The results in cc. are reported only to the first decimal place, as beyond that they have no significance.

Trial IV.—To determine the effect of adding to the flour extract 50 mg., respectively, of potassium dihydrogen phosphate, potassium hydrogen phosphate, or potassium orthophosphate, for each 10 g. of flour, extracted, and digesting at 40°.

Potassium Dihydrogen Phosphate is acid and the amount of $\text{Ba}(\text{OH})_2$ neutralized in the first stage is very much increased. In Trial III the amount of 0.05 N $\text{Ba}(\text{OH})_2$ neutralized in the blank for the first stage was 3.3 cc. and here it was 12.7 cc. The 9.4 cc. $\text{Ba}(\text{OH})_2$ was neutralized by the 50 mg. KH_2PO_4 . The amount of titrable nitrogen increases during the first two weeks, but the increase is not materially different from the results obtained when only neutral water was used, showing that this salt has no catalytic action on protein cleavage. If there is any influence it is retarding.

TABLE IV.—EFFECT OF POTASSIUM PHOSPHATES.

Time.	1st stage. Cc. 0.05 N $\text{Ba}(\text{OH})_2$.	2nd stage. Cc. 0.05 N $\text{Ba}(\text{OH})_2$.	Milligrams N in amino form.
Potassium Dihydrogen Phosphate.			
blank	12.7	2.6	1.82
24 hours	12.5	2.9	2.03
1 week	12.4	4.8	3.36
2 weeks	12.7	5.6	3.92
3 weeks	12.7	5.4	3.78
4 weeks	12.1	5.7	3.99
5 weeks	12.5	5.2	3.64
Potassium Hydrogen Phosphate.			
blank	2.4	3.3	2.31
1 week	2.9	4.3	3.01
2 weeks	4.4	4.0	2.80
3 weeks	4.4	4.2	2.94
4 weeks	4.6	4.1	2.87
5 weeks	5.0	4.4	3.08
6 weeks	5.1	4.4	3.08
Potassium Orthophosphate.			
blank	0.4 ¹	3.2	2.24
1 week	0.0	4.2	2.94
2 weeks	0.6	4.6	3.22
3 weeks	0.7	5.1	3.75
4 weeks	1.2	5.2	3.64
5 weeks	1.5	4.5	3.15
6 weeks	1.8	5.0	3.50
7 weeks	1.7	5.3	3.71
8 weeks	2.0	5.9	4.13

¹ 0.4 HCl added.

Potassium Hydrogen Phosphate was slightly basic as shown by the fact that the blank titration for the first stage is a little less than in Trial III. This basicity decreases slowly but definitely. The amount of titrable nitrogen shows no increase after the first week. This salt has, therefore, in the amount used, an inhibiting effect on protein cleavage.

Potassium Orthophosphate is basic, and the addition of this amount of salt is more than sufficient to neutralize the acidity of the flour extract as shown by the titration of the blank. The acidity of the flour extract is probably due to the presence of salts similar to KH_2PO_4 , judging from the amount of bases and phosphorus present. The addition of K_3PO_4 would react with the KH_2PO_4 , forming K_2HPO_4 , which, as shown, is almost neutral or only slightly basic. The basicity decreases. At the end of the first week the extract was neutral to phenolphthalein, and the acidity gradually increased. The K_3PO_4 has a retarding effect on protein cleavage.

Trial V.—To determine the effect of adding to the flour extract 80 mg. KOH for every 10 g. of flour extracted. This made the solution alkaline.

TABLE V.—EFFECT OF ADDING POTASSIUM HYDROXIDE.

Time.	1st stage.	2nd stage.	Milligrams
	Cc. 0.05 N HCl.	Cc. 0.05 N $\text{Ba}(\text{OH})_2$.	N in amino form.
blank	14.6	3.4	2.38
1 week	9.6	3.4	2.39
2 weeks	7.3	3.3	2.31
3 weeks	7.1	4.0	2.82
4 weeks	6.5	3.3	2.31
5 weeks	6.2	3.0	2.10
6 weeks	5.0	2.8	1.96
7 weeks	5.1	2.4	1.68
8 weeks	5.4	2.6	1.82

The alkalinity decreases regularly till the end of the fifth week. The result is very similar to that obtained in Trial IV with K_3PO_4 . It may mean that more KH_2PO_4 is formed through hydrolytic action. The amount of titrable nitrogen does not increase, showing that the presence of this amount of KOH stops protein cleavage.

Trial VI.—To determine the effect of adding 100 mg. K_2S for each 10 g. of flour extracted. The effect of this salt was a slight increase in the acidity during the first week, after which the results were constant. The increase in the amount of titrable nitrogen is not greater than when water

TABLE VI.—EFFECT OF ADDING POTASSIUM SULFIDE.

Time.	1st stage.	2nd stage.	Milligrams
	Cc. 0.05 N $\text{Ba}(\text{OH})_2$.	Cc. 0.05 N $\text{Ba}(\text{OH})_2$.	N in amino form.
blank	4.7	3.1	2.17
1 week	7.5	3.8	2.66
2 weeks	7.9	4.6	3.22
3 weeks	7.4	6.0	4.20
4 weeks	7.2	6.2	4.34

alone was used, showing that K_2S in the amount used, has no influence on the rate of protein cleavage.

Trial VII.—To determine the effect of adding to the flour extract 50 mg. of NH_4Cl for each 10 g. of flour extracted. There was no notable change in the amount of titrable material obtained in the first stage until after the fourth week. The amount of titrable nitrogen obtained in the second stage was large. The great increase in the blank is due to the presence of ammonia.

TABLE VII.—EFFECT OF ADDING AMMONIUM CHLORIDE.

Time.	1st stage.	2nd stage.	Mg. N in amino form, due to presence of NH_4Cl .
	Cc. 0.05 N $Ba(OH)_2$.	Cc. 0.05 N $Ba(OH)_2$.	
blank	4.7	21.0	12.70
1 week	4.7	23.7	14.59
2 weeks	5.1	26.0	16.20
3 weeks	4.7	28.0	17.60
4 weeks	4.9	29.2	18.44
5 weeks	7.0	34.2	21.94

The presence of NH_4Cl increases the amount of protein cleavage more than any of the previous salts used in this series of experiments. The average mg. nitrogen obtained in the blanks of the preceding trials is very nearly 2. The increase beyond this amount is due to the presence of the NH_4Cl .

Trial VIII.—To determine the effect of adding to the flour extract 50 mg. of $CaCl_2$ for each 10 g. of flour extracted. The amount of titrable material obtained in the first stage shows a very slight increase during the first week.

TABLE VIII.—EFFECT OF ADDING CALCIUM CHLORIDE.

Time.	1st stage.	2nd stage.	Milligrams N in amino form.
	Cc. 0.05 N $Ba(OH)_2$.	Cc. 0.05 N $Ba(OH)_2$.	
blank	3.6	2.6	1.82
1 week	4.2	5.2	3.64
2 weeks	4.5	7.2	5.04
3 weeks	5.4	11.0	7.70
4 weeks	5.2	13.5	9.45
5 weeks	4.4	14.7	10.29

The amount of titrable nitrogen obtained in the second stage shows that $CaCl_2$ is practically equal to NH_4Cl in affecting the rate of protein cleavage.

Trial IX.—To determine the effect of adding to the flour extract HCl , in such amounts as to make the concentration of the solution equivalent to 0.01 N. As it would take 20 cc. of the 0.05 N $Ba(OH)_2$ to neutralize the HCl present in the 100 cc. portion titrated, the difference between 20 and the figures given shows the amount of $Ba(OH)_2$ neutralized by the substances present in the flour extract. These figures are very nearly the same as would be obtained in titrating the flour extract alone as in

Trial III. The amount of titrable nitrogen obtained in the second stage shows that at this concentration HCl inhibited protein cleavage.

TABLE IX.—EFFECT OF ADDING HCl.

Time.	1st stage.	2nd stage.	Milligrams N in amino form.
	Cc. 0.05 N Ba(OH) ₂ .	Cc. 0.05 N Ba(OH) ₂ .	
blank	22.44	2.40	1.68
1 week	23.44	3.45	2.42
2 weeks	23.12	3.10	2.17
3 weeks	23.00	3.80	2.66
4 weeks	23.10	4.10	2.87

Trial X.—To determine the effect of adding to the flour extract HCl in such amounts as to make the concentration equivalent to 0.1 N. It would require 200 cc. of the 0.05 N Ba(OH)₂ solution to neutralize the HCl present in the 100 cc. portions titrated. In addition to this it would take about 2.5 cc. 0.05 N Ba(OH)₂ to neutralize the substances in the flour extract. The figures show that it required only 196 cc. Ba(OH)₂. This means that the equivalent of 6.5 cc. 0.05 N HCl was absorbed or neutralized by the substances in the flour extract. The HCl at this concentration completely inhibits protein cleavage.

TABLE X.—EFFECT OF ADDING HCl EQUIVALENT TO A CONCENTRATION OF 0.1 N.

Time.	1st stage.	2nd stage.	Milligrams N in amino form.
	Cc. 0.05 N Ba(OH) ₂ .	Cc. 0.05 N Ba(OH) ₂ .	
blank	196.0	3.3	2.3
1 week	196.0	2.0	1.4
2 weeks	196.0	2.0	1.4
3 weeks	196.0	2.0	1.4

Effect of Adding Organic Substances.

Trial XI.—To determine the effect of adding to the flour extract 1.25 grams of desiccated egg albumen for each 10 g. of flour extracted.

TABLE XI.—EFFECT OF ADDING EGG ALBUMEN.

Time.	1st stage.	2nd stage.	Milligrams N in amino form.
	Cc. 0.05 N Ba(OH) ₂ .	Cc. 0.05 N Ba(OH) ₂ .	
blank	3.0	10.2	7.14
1 week	2.9	10.7	7.49
2 weeks	2.9	11.4	7.98
3 weeks	2.9	11.7	8.19

The egg albumen has no effect on the amount of titrable material obtained in the first stage. The amount of titrable nitrogen obtained in the second stage shows a small increase in protein cleavage, but this is not as great as would be obtained were egg albumen not present. The amount of titrable nitrogen obtained in the blank shows that the protein in the desiccated egg albumen has a large amount of nitrogen in the amino form.

Trial XII.—To determine the effect of digesting desiccated egg albumen in water, adding the egg albumen at the rate of 1.25 g. for every 100 cc. Egg albumen mixed with water has a slightly acid reaction, as shown

TABLE XII.—DIGESTING ALBUMEN IN WATER.

Time.	1st stage.	2nd stage.	Milligrams
	Cc. 0.05 N Ba(OH) ₂ .	Cc. 0.05 N Ba(OH) ₂ .	N in amino form.
blank	1.6	10.6	7.42
1 week	1.5	8.9	6.23
2 weeks	1.7	11.2	7.84
3 weeks	1.9	10.9	7.63
4 weeks	2.1	11.0	7.70

by the figures obtained in the first stage titration. This acidity apparently increases during the progress of digestion. The amount of titrable material obtained in the second stage does not show any regular increase or decrease.

Trial XIII.—To determine the effect of adding to the flour extract 1.25 g. of desiccated egg albumen for each 10 g. of flour extracted, and digesting at 40°. The amount of titrable material obtained in the first stage was greater than when the digestion was conducted at the lower temperature. It shows no marked increase beyond the first week. The amount of titrable nitrogen obtained in the second stage is more than doubled in the five weeks. This trial, in connection with Trial XI, shows that 40° is a much more favorable temperature for protein cleavage than room temperature. If the figures in Table XIII are compared with those in Table III, it will be observed that the protein cleavage goes on at a much greater rate when protein from egg albumen is present in the extract. This may be due in part, at least, to the greater concentration of the protein.

TABLE XIII.—EFFECT OF ADDING EGG ALBUMEN AND DIGESTING AT 40°.

Time.	1st stage.	2nd stage.	Milligrams
	Cc. 0.05 N Ba(OH) ₂ .	Cc. 0.05 N Ba(OH) ₂ .	N in amino form.
blank	4.9	10.3	7.21
1 week	5.6	14.6	10.21
2 weeks	5.5	16.1	11.27
3 weeks	5.2	19.2	13.44
4 weeks	5.0	21.9	15.33
5 weeks	5.4	23.8	16.66

Trial XIV.—To determine the effect of digesting desiccated egg albumen in water at 40°, adding the egg albumen at the rate of 1.25 g. for each 100 cc. The amount of titrable material obtained in the first stage is less than when the digestion was conducted at room temperature.

TABLE XIV.—DIGESTING EGG ALBUMEN IN WATER AT 40°.

Time.	1st stage.	2nd stage.	Milligrams
	Cc. 0.05 N Ba(OH) ₂ .	Cc. 0.05 N Ba(OH) ₂ .	N in amino form.
blank	1.30	9.40	6.58
1 week	1.30	9.40	6.58
2 weeks	1.50	9.50	6.65
3 weeks	1.30	9.80	6.86

There is no increase as the time of digestion is increased. The amount of titrable nitrogen obtained in the second stage is somewhat less than when the digestion was conducted at room temperature, and there is no increase.

Trial XV.—To determine the effect of adding to flour extract 1.25 g. of casein for each 10 g. of flour extracted, and digesting at 40°. A weighed amount of buttermilk casein was dissolved in the minimum amount of NaOH solution. This made a neutral solution of sodium caseinate. After filtering it was added to flour in such proportions that each 100 cc. contained 1.25 g. of casein. The titrable material obtained in the first stage is almost the same as when the flour extract was titrated, showing that the sodium caseinate was neutral. The acidity increases slowly but regularly. The amount of titrable nitrogen obtained in the blank for the second stage shows that casein has a larger amount of nitrogen in the free amino group than has the egg albumen. The amount of

TABLE XV.—EFFECT OF ADDING CASEIN AND DIGESTING AT 40°.

Time.	1st stage. Cc. 0.05 N Ba(OH) ₂ .	2nd stage. Cc. 0.05 N Ba(OH) ₂ .	Milligrams N in amino form.
blank	3.7	13.4	9.38
1 week	5.1	13.7	9.59
2 weeks	5.8	14.9	10.43
3 weeks	6.9	16.6	11.62
4 weeks	7.1	16.9	11.83

increase in the titrable nitrogen as the digestion progresses is no more than was obtained with the flour extract alone in Trial III, showing that the presence of protein from the casein does not cause a more rapid rate of protein cleavage, as was the case when the protein from egg albumen was present.

A fair question is: Are the observed changes due to proteolytic enzymes, or are they simply the result of hydrolytic action of water, or are they due to bacterial action? We believe that we have eliminated bacterial action, because in preliminary trials we compared the use of different amounts of toluene with results essentially the same. We judged the amount to be used by the technique followed by American and European workers. We believe that the changes observed are due to proteolytic enzymes and not to the hydrolytic action of water alone, because the observed changes were according to the generally observed behavior of enzymes in respect to activators, inhibitors, and action on other proteins, such as egg albumen.

Summary.

This paper presents the results of a study on certain conditions which affect the activity of proteolytic enzymes in wheat flour. It describes the use of the formal titration in determining the amount of nitrogen in the amino form present in flour, and also its use as a means of measuring protein cleavage due to proteolytic enzymes present in the flour. Of the

various salts tried, NH_4Cl and CaCl_2 had the greatest accelerating effect on the rate of protein cleavage. The proteolytic enzymes present in wheat flour caused a more rapid hydrolysis of the proteins when desiccated egg albumen was present, but not when casein was used.

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[CONTRIBUTION FROM THE ORGANIC LABORATORY, COLUMBIA UNIVERSITY AND THE HARRIMAN RESEARCH LABORATORY No. 263.]

ADSORPTION OF INVERTASE.

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Hedin and his collaborators, Jahnson-Blohm, and Eriksson,¹ found that the presence of certain substances like serum, egg albumin, saponin, cholestrin, and in some cases the substrate itself, lessened the inhibition of the activity of enzymes like rennet, trypsin and invertase. brought about by the presence of solid powders (charcoal), or substances soluble in water as colloids (serum and egg albumin). They considered this inhibition as due to the adsorption and removal of the enzyme from the sphere of action by the charcoal or serum. When, however, certain substances capable of being adsorbed by the inhibitor are present or added to the reaction mixture, they can replace part or all of the enzyme in the enzyme-adsorbent, and the liberated enzyme becoming active again, decreases the amount of inhibition.

It has been shown in a previous paper² that, although charcoal does adsorb invertase (and possibly serum and egg albumin do likewise), the apparent inhibiting effect is not due to this, but to a change in the hydrogen ion concentration of the reaction mixture produced by the charcoal, etc. In the light of these results, the explanation given by Hedin for the decrease in inhibition is untenable in the case of invertase at least, since the activity is independent of whether the invertase is adsorbed or not. This is further substantiated by the results indicated below, where the addition of a second substance such as saponin, serum or egg albumin to the enzyme-inhibitor mixture does affect the amount of invertase adsorbed by an inhibitor like charcoal or aluminium hydroxide. In no case is there any noticeable change in the activity as long as the hydrogen ion concentration is kept constant by means of suitable buffers.

Since very little experimental data were given in the previous paper concerning the activity of invertase while adsorbed by charcoal and gelatinous aluminium hydroxide, and since the results have an important bearing on the chemistry of enzyme action in general, as can be seen from the statements based on Hedin's conclusions, occurring in many text-

¹ *Z. Physiol. Chem.*, 72, 324 (1911); 82, 175, 178 (1912).

² THIS JOURNAL, 38, 722 (1916).

books,¹ it was deemed advisable to include in this paper a description of the following experiments:

Solutions A, B, C and D contained 100 cc. of a 10% cane sugar solution, 10 cc. of an invertase solution, and 20 cc. of a buffer solution which would give the desired hydrogen ion concentration, and 0.3 g. of finely powdered animal charcoal.

In the case of E, 0.6 g. of the charcoal, 40 cc. of buffer and 20 cc. of invertase solution were allowed to stand for one hour after first being thoroughly mixed, then filtered and 30 cc. of the filtrate added to the 100 cc. of the cane sugar solution.

Solution F was made up similarly to A except that no charcoal was used, and served as a control.

B, C and D were filtered after the inversion had progressed for certain lengths of time, and the amount of inversion in the filtrate compared with that of the unfiltered solution A, as well as with that of the control F.

Solutions G, H and I and J were similar to A, B, C and D, except that instead of the charcoal and buffer, 20 cc. of a suspension of gelatinous aluminium hydroxide, equivalent to 0.12 g. of aluminium oxide, were used.

TABLE I.

Solution.	+ p _H	Change in degrees of rotation after			
		18 hours.	24 hours.	42 hours.	48 hours.
A.....	5.3	4.15	5.40	8.21	8.70
B.....	5.3	4.02 ²	4.34	4.95	5.20
C.....	5.3	..	5.36 ²	5.86	6.04
D.....	5.3	8.17 ²	8.28
E.....	5.3	0.40	0.58	1.03	1.20
F.....	5.3	4.14	5.42	8.27	8.77
G.....	4.95	4.74	6.08	8.87	9.49
H.....	4.95	4.82 ²	4.82	4.85	4.87
I.....	4.95	..	6.07 ²	6.09	6.10
J.....	4.95	8.95 ²	8.97
K.....	4.95	0.01	0.02	0.05	0.06
L.....	5.0	4.80	6.13	8.99	9.63
		13 hours.	38 hours.	64 hours.	88 hours.
M.....	7.5	0.22	0.48	0.56	..
N.....	7.5	0.23 ²	0.22	0.25	..
O.....	7.5	..	0.45 ²	0.44	0.48
P.....	7.5	0.52 ²	0.52
Q.....	7.5	0.01	0.01	0.01	..
R.....	7.5	0.24	0.47	0.60	..

¹ "General Chemistry of the Enzymes," Euler, Wiley & Sons, 1912, p. 77, 81 and 82. "The Nature of Enzyme Action," Bayliss, 2nd ed., p. 105. "Die Fermente und ihre Wirkungen," Oppenheimer, Leipzig, 1913, p. 79. "Physikalische chemie der Zelle und Gewebe," Höber, 4th ed., p. 738, and others.

² Indicates the time when the adsorbent was removed by filtration.

Solution K corresponded to E, except that 30 cc. of a filtrate from a mixture of 40 cc. aluminium hydroxide and 20 cc. of invertase solution was used in place of the filtrate described under E.

Solution L served as a control for G, H, I and J and differed from them in that it contained 20 cc. of a buffer solution (sodium citrate and hydrochloric acid), instead of the aluminium hydroxide.

Solutions M, N, O, P, Q and R only differed from solutions G, H, I, J, K and L in having a lower hydrogen ion concentration, $p_H^+ = 7.5$ instead of 4.9. The change in hydrogen ion concentration was brought about by adding 10 cc. of 0.1 *M* hydrochloric acid to 150 cc. of the aluminium hydroxide suspension used for Solutions G, H, I and J.

On comparing the values from A, G and M with those from the respective controls, F, L and R, containing no adsorbent E, it is apparent that the presence of the latter is without effect on the rate of inversion. The values for G and M show that the same holds for solutions containing different hydrogen ion concentrations. Values for B, C, D, H, I, J, N, O and P show that the enzyme is practically removed (especially when aluminium hydroxide was used), by filtering off the adsorbent, since the filtrates show no appreciable additional change in rotation.

Since the charcoal and aluminium hydroxide carrying the invertase settled to the bottom of the bottle in which the inversion was taking place, it became evident that it made no difference whether the enzyme was uniformly distributed throughout the solution or not. This behavior agrees with the opinion held by many that enzymes are colloids, and that the action between the invertase and cane sugar solution depends on the contact of the cane sugar solution with the insoluble enzyme, either in suspension or adsorbed to the charcoal or aluminium hydroxide. The simplest way to account for the uniformity in activity when the enzyme occurs in the bottom of the bottle in an adsorbed state as when uniformly suspended throughout the entire system, is that the inversion depends on an interaction between two distinct phases, where the amount of surface of contact between the enzyme phase and cane sugar phase remains constant. Why the extent of the enzyme phase exposed to the cane sugar phase should appear to be the same in the adsorbed condition as when it is uniformly distributed throughout the solution, is at present hard to say. If the idea of the amount of surface contact between the two phases is correct, then the surface area of the invertase particles must be constant under the same hydrogen ion concentrations, since so many workers have found a definite ratio to exist between the amount of invertase used and the rate of inversion. This also brings up the question whether the concentration of the hydrogen ion is the same on the surface of the charcoal as it is in the solution. Another question which suggests itself is: Is the size of the enzyme particles dependent on the hydrogen ion

concentration of the cane sugar solution in which the inversion is taking place? To the latter question Bayliss¹ has ventured the answer that it does. In this communication Bayliss also points out an argument for the view that enzymes are of colloidal nature, since there are cases where the enzymes have been insoluble in the solution of the substrate and still were active. This is in agreement with the results described above.

The following series of experiments were undertaken to study whether substances like saponin and egg albumin might have any influence on the activity of invertase in the presence of an adsorbent such as charcoal or egg albumin, as claimed by Hedin and his co-workers.

For this purpose the following solutions were prepared: Solutions I and II consisted of 70 cc. of water, 1 g. of finely powdered animal charcoal, 20 cc. of a buffer solution, and 10 cc. of invertase. Solution III. This solution was similar to I and II, except it contained 45 cc. of water instead of 70.

One gram of saponin was added to II, and 25 cc. of a 20% egg albumin solution (in which $p_H^+ = 5.1$), to III. Each of these solutions, II and III, were then divided into three separate portions and marked IA, IB, IC, IIA, IIB, IIC, IIIA, IIIB, and IIIC. All of the B mixtures were filtered and 20 cc. of the filtrate added to 80 cc. of a 10% cane sugar solution. All of the A mixtures were centrifuged instead of filtered, in order to show that the process of filtering had no influence on the activity of the invertase, and 20 cc. of the supernatant liquid added to 80 cc. of 10% cane sugar solution. In the case of all the C mixtures, 20 cc. of the original was added directly to the 80 cc. of 10% cane sugar solution.

TABLE II.

Solutions.	IA.	IB.	IC.	IIA.	IIB.	IIC.	IIIA.	IIIB.	IIIC.
p_H^+	6.6	6.6	6.7	6.4	6.4	6.5	6.0	6.0	6.1
Change in rotation after									
20 hours	0.02°	0.01°	0.75°	0.86°	0.88°	0.82°	1.22°	1.20°	1.16°
After 48 hours	0.01°	0.00°	1.59°	1.77°	1.82°	1.67°	3.15°	3.13°	3.00°

The values obtained from solutions IA and IB, when compared with those from IC, show that on filtering or centrifuging off the charcoal, when no saponin or egg albumin was present, the invertase was also removed. The values from IIA, IIB, IIIA and IIIB show that the presence of both the saponin and egg albumin prevented the charcoal from removing the invertase, and in this respect the results agree with the claims of Hedin and Jahnson-Blohm. A comparison of the values from IIA and IIB with those from IIC, and the values from IIIA and IIIB with those from IIIC, shows that, even when the saponin prevents the adsorption of the invertase by the charcoal, no effect is noticeable on the activity. This behavior of the saponin and egg albumin indicates that they act as

¹ *Science*, 42, 513 (1915).

protective colloids towards the invertase, and according to the present theories concerning protective colloids, the invertase is therefore adsorbed to the saponin and egg albumin as well, which is contrary to the views of Hedin and co-workers. Therefore it seems that the invertase adsorbed to colloids like saponin and egg albumin behaves in a manner similar to that adsorbed to charcoal, and in each case the activity is not affected. It furthermore indicates that the adsorption of invertase to charcoal is influenced by these protective colloids in a way similar to the coagulation of metal sols, etc. If this is so, and if activity is dependent on the amount of surface of the enzyme particles, we might then have an additional property to aid us in the study of the relationship existing between the adsorbent and the substance adsorbed in the adsorption combination.

Since all preparations of invertase whose composition have been examined always contained a polysaccharide and probably a protein, both of which substances would very likely act as protective colloids, the possibility suggests itself, that the true invertase principle might be something adsorbed to this material. For this reason, some gelatinous aluminium hydroxide, free from nitrogen, was added to an invertase solution whose nitrogen content was known. The aluminium hydroxide was subsequently filtered off, and the amount of nitrogen in the filtrate again determined, as well as the activity of the aluminium hydroxide, containing the adsorbed invertase, and the amount of nitrogen it carried with it. It was thought that it might be possible that only the active principle might be adsorbed to the aluminium hydroxide, and if it were nitrogen free, this fact would be revealed. The aluminium hydroxide however did carry with it some nitrogenous material and therefore no definite conclusions could be drawn.

Jahnson-Blohm¹ claimed that the addition of saponin or egg albumin as the second colloid to a mixture of rennet or trypsin and their respective substrates containing serum or egg albumin, also affected the activity of the enzymes just as when charcoal was used as the adsorbent.

In order to see whether any effect of this kind occurred when an invertase cane sugar solution, containing serum or egg albumin, was treated with saponin or egg albumin as the second colloid, the following experiments were undertaken. The results obtained again show that in the case of invertase, there is no such effect on the activity produced by this addition of a second colloid.

The solutions used in these experiments were:

A. Ten cc. of invertase solution, 5 cc. of a 25% serum solution, in which the serum had been neutralized previously with 0.1 molar hydrochloric acid to $p_H^+ = 6.8$, were mixed and allowed to stand for some time, and then added to 5 cc. of water and 50 cc. of a 20% cane sugar solution.

¹ *Loc. cit.*

B and C differed from A in having 5 cc. of 1% saponin solution and 5 cc. of a 20% egg albumin solution, respectively, in place of the 5 cc. of water in A. D, E and F were controls for A, B, and C, respectively, and contained 10 cc. of buffer solution in place of the 5 cc. of serum and 5 cc. of water in A, in order to give them the same hydrogen ion concentration.

TABLE III.

Solutions.	A.	D.	B.	E.	C.	F.
α_D^{20}	7.1	7.1	7.0	7.0	6.4	6.4
Change in rotation after 18 hours.....	2.02°	2.04°	2.12°	2.15°	2.77°	2.75°

In these solutions serum was used as the first colloid or adsorbent. The value obtained from A, where the second colloid was absent, agrees with its control, D, containing no serum. The values of B and C, which contained both the first colloid or adsorbent (serum), and the second colloid (saponin and egg albumin, respectively), also are the same as those of the controls E and F, which contain no saponin, egg albumin nor serum. It is therefore evident that the presence of one or more colloids does not affect the activity of invertase.

Similar results were obtained when the order in which these three substances, serum, egg albumin and saponin were mixed, was interchanged. Thus when invertase and egg albumin were permitted to stand for some time and then saponin or serum added, no difference in the activity of the enzyme was noticed.

Eriksson¹ found that the inhibition became less as the length of time before filtering increased when the cane sugar solution was added to a mixture of charcoal and invertase in water, which had stood for some time to allow the charcoal to adsorb the enzyme, and then filtering off the charcoal after different lengths of time after the substrate had been added. This he considered due to the cane sugar gradually liberating the invertase adsorbed to the charcoal and again becoming active.

Explained in the light of the results indicated in this and previous papers,² the filtering off of the charcoal would carry with it some of the invertase, and the longer this invertase adsorbed to the charcoal was permitted to be in contact with the sugar solution, the greater would be the amount of inversion taking place, and therefore there is no indication whatever that the cane sugar liberates the invertase from the charcoal-invertase combination.

For a description of the methods employed in making the above measurements, etc., see Experimental Part in previous paper.³

¹ *Loc. cit.*

² THIS JOURNAL, 38, 722 (1916).

³ *Ibid.*, 38, 722 (1916).

Summary.

1. It has been shown, in a new way, that invertase is colloidal in nature, and the reaction between the enzyme and cane sugar solution depends on the contact of two phases.
2. The activity of invertase (the product obtained from yeast and called invertase), is not affected whether or not the enzyme is adsorbed to a solid like charcoal, or to a colloid like saponin, serum, or egg albumin, distributed uniformly throughout the solution of the substrate.
3. Displacing the adsorbed invertase by a second colloid is without effect on the activity, contrary to the views held by many.
4. Invertase can be removed from an aqueous solution by adsorption to a solid, and again brought into solution by a second colloid suspended uniformly throughout the solution.
5. Eriksson's proof that cane sugar can liberate invertase adsorbed to charcoal is not valid.

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THE RESEARCH LABORATORY OF ARMOUR AND COMPANY.]

ON THE REACTION OF THE PANCREAS AND OTHER ORGANS.

[SECOND PAPER.]

By J. H. LONG AND F. FENNER.

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In a recent paper¹ we showed that the "press juice" obtained from the pancreas of the hog, sheep and beef by centrifugal separation, is characteristically acid, the degree of acidity being nearly constant. This unexpected result suggested the importance of further experimentation, as it has usually been assumed that the reaction of the fluids of the body is not far from that of the serum. But this assumption leaves out of consideration the fact that the external secretion of the pancreas is rather markedly alkaline. A compensating acidity should then be expected somewhere, and most naturally within the organ.

In our view the reaction might be due, in part at least, to the presence of acid phosphates in the juice, or possibly to acid organic compounds of phosphoric acid, since the acid is abundantly present. In the discussion following the presentation of the paper at the Seattle meeting, Sept. 1, 1915, the suggestion was made by several colleagues that the acidity might be due to ferment action through the lipase present. This and other points had already been considered by us, but in view of the importance of the phenomenon we have thought it desirable to present further evidence bearing on the question, this evidence being in the form of data collected since the first paper was published.

¹ THIS JOURNAL, 37, 2213 (1915).

It was pointed out in that paper that the organs taken immediately from the animal after death exhibit an acid reaction with litmus. This was followed up in various ways. In the month of September the test was made on the organs of 160 sheep, 200 cattle and 120 hogs by one of us and assistants, the organs being cut open and tested while still warm. This of course precluded the possibility of acid formation through ferment action. An acid behavior was always found. The same fact may be shown in a very convincing form in this manner. A mixture of from 20 to 50 g. of the minced organ and some sodium bicarbonate is stirred up in the bottom of a beaker. Soon the mass begins to rise and may even flow over the top of the vessel, from the liberation of carbon dioxide. Certain proteins, it must be remembered, show the same behavior; casein for example. These proteins are acid in character.

It was evident from these and other observations that the acid reaction is present in the fresh organs and is not a consequence of bacterial decomposition, which might follow if the organs were allowed to stand some time before the tests were completed.

Since the tests recorded in the earlier paper were made on the juice of animals killed during the summer, mostly in July, it was thought wise to collect organs during the fall and early winter months for comparison. The results obtained under these conditions are given below. In the first of the observations the same Hasselbalch cells and platinized electrodes were used that were employed before. Experiments were frequently made with phosphate solutions of known hydrogen ion concentration for control. Then new electrodes with fresh deposits were substituted, tested by phosphate and other control solutions and used in the later work. In some of the observations toward the end of the series the cell recently described by one of us¹ was employed. The results obtained with it were always in close agreement with those from the first named cell. The data for the different pancreases tested will now be given, and in each case with date and number:

No. 123, Sept. 27. Beef pancreas. Organs placed in refrigerator immediately after removal from animal. Temperature 0°. Minced next morning and the juice separated by the centrifuge at once. Marked reddish color.

No. 124, Sept. 27. Hog pancreas. Condition the same as for No. 123.

No. 125, Sept. 29. Beef pancreas. Organs brought to laboratory and juice separated without delay.

No. 126, Sept. 29. Sheep pancreas. Conditions as in No. 125.

No. 127, Sept. 30. Sheep pancreas. Immediate separation of juice.

No. 128, Sept. 30. Hog pancreas. Immediate separation of juice.

No. 129, Oct. 1. Sheep pancreas. The fat was thoroughly trimmed off and the organs thrown into boiling water. After boiling 15 minutes the glands were minced and centrifuged. It was found necessary to add a little water to aid in the separation. The reaction of the liquid now obtained was found to be slightly acid to litmus, more

¹ THIS JOURNAL, 38, 936 (1916).

acid than 6 sec. phosphate plus 4 prim. phosphate. The juice included some of the added water, and probably held more or less of the β -proteid of Hammarsten, to be discussed later.

No. 130, Oct. 1. Hog pancreas. Conditions as for No. 129.

No. 131, Oct. 6. Hog pancreas. The fresh juice was tested in parallel with a borate solution as control, with all conditions identical.

After making the observations on the liquids described above the platinum electrodes were cleaned and recoated. Before doing this, however, the potential values were found in a standard phosphate mixture as a control. This mixture was composed of equal volumes of molar/15th primary and secondary phosphates, as suggested by Soerensen. For the two cells we found $\pi = 0.7357$ and 0.7339 , at 21° , or $P_H = 6.813$ and 6.783 . After recoating we found the cells uniform with $P_H = 6.784$, which is a very satisfactory situation. More pancreas examinations were then made:

No. 141, Dec. 21. Hog pancreas. A large number of glands were minced and a mixture of juices from four centrifuge tubes taken for tests.

No. 142, Dec. 21. Hog pancreas. Juice obtained from another large lot of glands to secure averages. The liquids were separated in the forenoon and delivered for the potential determinations before 1.30 P.M.

The potential determinations on all these centrifugal juices are given below. It will be seen that they are fairly constant and agree pretty closely with the results of our former paper. It is believed that we have enough individual tests to properly cover the seasonal and other variations. The numerical values are given in Table I.

TABLE I.

No.	Animal.	Potential.	P_H .	Cm.
123	Beef	0.6691	5.691	20.3×10^{-7}
124	Hog	0.6690	5.689	20.5
125	Beef	0.6710	5.705	19.7
126	Sheep	0.6709	5.704	19.8
127	Sheep	0.6691	5.691	20.3
128	Hog	0.6690	5.689	20.5
129	Sheep	0.6970	6.170	6.7 boiled liquid
130	Hog	0.7261	6.670	2.1 boiled liquid
131	Hog	0.6679	5.685	20.7
141	Hog	0.6666	5.641	22.8
142	Hog	0.6633	5.591	25.6

Leaving out of consideration numbers 129 and 130, which are the liquids from the boiled organs and somewhat diluted, it will be seen that the results are remarkably uniform. The P_H values are a trifle higher than were those reported in our former paper for the hog and beef products, but a little lower than we found for the sheep, in the mean. Such variations follow, possibly, from differences in the completeness of extraction, which may depend, in part, on the temperatures reached in the centrif-

ugal machine. In any event they are almost within the limits of error in observation.

These results with the pancreas liquids suggested the importance of testing the juices from other organs, which, like body fluids in general, have all been assumed to have a nearly neutral reaction like the blood. The pancreas liquid is unquestionably acid; may not the same condition be found in other organs? We have made a number of examinations of the centrifugal juice from other minced organs, as follows:

No. 132, Oct. 15. Parotid gland of hog. A satisfactory separation could not be obtained, even after some hours of rapid rotation. The minced gland is rich in mucus which evidently interferes with such a separation as we secured from the pancreas. On mixing the minced mass with a little water, however, boiling and filtering, enough liquid was secured to make the potential tests. Similar efforts to secure liquids from the sub-lingual and sub-maxillary glands were not successful, as these glands furnish a slimy mass only, which could not be filtered.

No. 133, Oct. 15. Beef parotid gland. Conditions were similar to those for No. 132. A liquid was obtained in the same way.

No. 134, Oct. 19. Beef parotid. In this case the minced gland was ground with fine washed quartz and a little water. After the centrifugal action a clear filtrate was obtained. Through this filtrate a stream of pure hydrogen was passed to drive out carbon dioxide possibly absorbed in the long preliminary treatment. The liquid was then forced into the potential cell by means of hydrogen gas pressure, avoiding contact with air. The potential found remained constant overnight.

No. 135, Oct. 26. Beef parotid. The glands were removed on the evening of the 25th and quickly frozen, remaining so overnight. They were then ground fine and centrifuged without addition of sand or water. A red liquid was obtained which evidently contained hemoglobin. Hydrogen was applied as in the last case before filling the potential cell.

Sub-lingual and sub-maxillary glands collected at the same time and treated in the same way gave a distinct acid reaction with litmus but could not be made to yield a clear juice.

No. 136, Nov. 1. Hog bile. Clear. Some of the liquid was tested immediately and some after standing 24 hours in the cold. This latter bile showed an increased alkaline reaction.

No. 137, Nov. 1. Hog bile. Markedly turbid. It was tested at once.

No. 138, Nov. 2. Sheep liver. A centrifugal separation from the freshly removed livers is rather easily secured. In this case the liquid was blood red. It was tested at once.

No. 139, Dec. 17. Hog thyroid. The centrifugal liquid was secured on the evening of the 16th and kept near the freezing point until the next morning when the test was made.

No. 140, Dec. 17. Hog liver. The liquid was separated on the evening of the 16th. The separation was comparatively easy.

No. 143, Dec. 22. Hog thyroid. Minced organ centrifuged in the morning and the reddish liquid obtained examined for the potential in the early afternoon.

No. 144, Dec. 22. Hog spleen. Treated and tested as 143.

No. 145, Dec. 22. Hog liver. Treated and tested as 143.

No. 146, Jan. 5. Hog spleen. Separation easy, treated and tested at once.

No. 147, Jan. 5. Beef spleen. Separated and tested at once.

In practically all the above cases, it is seen, the centrifugal liquid was not allowed to stand more than the time necessary to transfer from the centrifuge to the potential cell. Where the separation was made in the laboratory of the medical school this was but a few minutes, and where made in the laboratory of Armour & Company it was not above an hour. There was no time allowed in which fermentation changes could take place of sufficient importance to affect the potential results. The potential determinations are given in Table II.

TABLE II.

No.	Organ.	Potential.	P _H .	C _H .
132	Hog parotid	0.7339	6.804	1.57 × 10 ⁻⁷
133	Beef parotid	0.7064	6.332	4.66
134	Beef parotid	0.7187	6.545	2.85
135	Beef parotid	0.7169	6.512	3.07
136	Hog bile	0.7491	7.042	0.91
	Same, after standing	0.7668	7.369	0.43
137	Hog bile	0.7592	7.215	0.61
138	Sheep liver	0.7180	6.510	3.09
139	Hog thyroid	0.7505	7.089	0.81
140	Hog liver	0.6959	6.151	7.06
143	Hog thyroid	0.7524	7.099	0.80
144	Hog spleen	0.7093	6.361	4.35
145	Hog liver	0.6981	6.169	6.78
146	Hog spleen	0.7223	6.563	2.73
147	Beef spleen	0.7215	6.550	2.82

The examination of the liquids from other organs than the pancreas discloses the very interesting fact that a number of them are very distinctly acid, although not to the same degree that was found in the pancreas. In general, these juices do not appear to be as rich in the phosphates as we find for the pancreas juice.

The press juice from the salivary glands all appear to be slightly acid, although the saliva itself is usually described as alkaline. However, this alkaline reaction is never strong and is by no means constant. After a meal the flow of the mixed saliva may even be slightly acid. The reaction seems to vary with the gland from which the flow is secured. This being the case, we should expect to find at times an acid reaction in the gland cells to balance the corresponding alkaline flow to the mouth of the saliva proper. The same condition doubtless prevails here that we find in the pancreas. The nearly neutral blood furnishes the juice which appears both in the saliva and in the external excretion of the pancreas, the so-called pancreatic juice. When these are alkaline we should properly expect the return flow to the blood to be acid.

The reaction of the bile appears to be neutral, or very slightly alkaline. The numerical values obtain for a temperature of 20°, from which it appears that the observed reaction is about of the neutral order. We have

more than once observed that the bile becomes slightly alkaline on standing, and this change may be responsible for the view usually held. It is true that the bile is alkaline, in the sense that it contains salts of weak acids which by double decomposition are able to neutralize hydrochloric acid from the stomach, but free alkali is doubtless not present. According to Foa,¹ however, the bile may be at times appreciably acid. This might be expected when the conditions of the formation of bile are kept in mind.

In degree of acidity the liver appears to stand next to the pancreas. The juices from the two hog livers examined show an acidity about one-third of that noted in the pancreases, but the causes of the reaction in this case are doubtless different from what they are in the case of the latter organ. The work of the liver is so largely chemical, involving the production and combination of so many groups of acid character, that the resulting reaction may well be acid. It must be kept in mind, further, that the nucleoproteins abundantly present may play a part here as some of them are slightly acid. It is probable that the degree of acidity in the liver will be found to vary with the time of taking food.

The two specimens of thyroid juice obtained are practically neutral and in this respect resemble the bile. As the thyroid possesses no system of external secretion it is practically necessary that the reaction of its press juice should be very close to that of the blood. Of the essential work of the thyroid but little is known; however, any products formed must be contained in the press juice or must go back to the blood and the sum of the reactions cannot be well changed.

The spleen, on the contrary, discloses a slight degree of acidity, not greatly different from that of the parotid gland. In view of the relation of this organ to the blood and the absence of any clearly defined excretory system it is surprising that a reaction should be found which is in any essential different from that of the blood. One of the main functions of the spleen, perhaps the important function, is connected with the elaboration of the white blood corpuscles. It is possible that this operation involves the liberation of a slight trace of an acid fraction from the complexes from which the white cells are produced. If these cells themselves should be found to be on the slightly alkaline side the rejected material might well be slightly acid. In the building up of new cells from the amino acid complexes available such a rearrangement might possibly occur. It will be necessary to examine a much larger number of organs before the constancy of the acid behavior can be definitely affirmed.

The slight degrees of acidity or alkalinity observed in some of the cases discussed above are so near the neutral point that errors of experi-

¹ See "Neuberg's Handbuch," II, p. 1601.

ment must be always kept in mind. We have therefore made frequent controls of the apparatus and have used different types of cells in the progress of the work. In practically all cases the final readings were made by aid of a delicate D'Arsonval galvanometer as well as by the use of the capillary electrometer. To secure greater delicacy the cell and measuring apparatus were mounted on blocks of paraffin. A temperature of 20° was maintained as closely as possible throughout the experiments.

It is known that the removal of carbon dioxide from blood serum by a current of hydrogen causes an appreciable increase in the apparent (OH) concentration, which is in turn reduced by restoring the displaced gas. In our experiments the possible effect of carbon dioxide, absorbed from the laboratory air during manipulation, was tested by noting the changes in dilute potassium chloride solutions. Made up with fresh distilled water the P_H values of these solutions were always close to 7 at 20° . By exposing the potassium chloride solutions in beakers into which the breath was blown it was found possible to perceptibly reduce the potential and reach P_H values ranging from 6.8 to 6.9, indicating slight degrees of acidity. But the amount of contamination in such cases was far greater than would be possible in our usual experimentation, from which we conclude that an acidity error from the absorption of carbonic acid must be of a very low order and not sufficient to account for any of the values obtained.

In a very considerable number of cases the potential cells were allowed to stand overnight after the constant readings had been obtained. In the morning, at the same temperature, these readings were generally found to be quite unchanged, showing that reaction changes from ferment or other kind of activity were inappreciable. On the whole, we are of the opinion that the values recorded represent the actual normal reactions of the organs in question.

Source of the Acid Reaction of the Pancreas.

We do not intend in this place to attempt an explanation of the cause of the acidity observed in any case except that of the pancreas. From the preliminary tests made it was suggested in our earlier paper that the explanation of the pancreas reaction may be found possibly in the relation of the various phosphates in the centrifuge juice, that is in the proportions of the primary and secondary alkali phosphates. This can be determined only by a complete analysis of the inorganic substances in the liquid and allowance for the phosphorus organically combined. We have carried out such an analysis, to be given below.

It must be recognized, further, that some of the organic phosphorus compounds of the type of the nucleoproteins have an appreciable acidity

and the presence of such bodies may be a factor of importance. This point will be considered in what follows.

As regards the relation of the acid and basic groups among the salts of the extracted liquid it is probably true that, while the concentration of the extract may vary with the length of time given to the centrifugal action, the character of the reaction will depend mainly on the relation between the ions of the extract. The ions of the alkali phosphates form readily soluble salts which probably extract in equal degrees of rapidity. In the determination of the various ions present we examined a composite made from a portion of each fluid used in the potential measurements on the hog pancreas. The individual liquids making up the composite vary somewhat in their properties but the mixture undoubtedly well represents the average character of the press juice. In a former paper¹ it was shown that the solids in the liquid from the hog pancreas made up about 15% of the whole, while in the beef pancreas juice the solid part was somewhat less. We are concerned with the hog pancreas juice alone here, and the centrifugal actions may be described as of moderate length, and so conducted as to avoid much rise in temperature. To show the effect of temperature on the extract some other composites were made. The results from this large composite are here given in percentage form, that is as parts of the whole liquid.

Water.....			83.7%
Solids.....			16.3%
Proteins (N = 2.1).....	13.09	Calcium, Ca.....	0.026
Ash.....	1.32	Magnesium, Mg.....	0.020
Phosphoric acid, PO ₄	0.982	Potassium, K.....	0.328
Chlorine, Cl.....	0.012	Sodium, Na.....	0.121
Sulfuric acid, SO ₄	0.000		

As the ash must contain the phosphates in condensed type, meta- or pyrophosphates, its weight appears small in comparison with the sum of the weights of the phosphoric acid and the metals. The composition of this liquid is somewhat remarkable. While the total solid matter is less than is found in the blood, for example, the salt fraction is unusually high, apparently much higher than is found in any other of the body fluids. The relatively high content of potassium is to be noted. It was separated from the sodium by chloroplatinic acid, and determined, also, indirectly a number of times.

The phosphoric acid is the total acid, that contained in the nuclein form as well as in combination with metals. While the liquid contains a trace of sulfur, it appears to be all in protein combination, and not in the oxidized form as sulfate. The trace of sulfur in the ash is not calculated as sulfate. The low chlorine content is noteworthy and was reached

¹ THIS JOURNAL, 37, 2427 (1915).

in a number of determinations, as well as with different composites. The amount found corresponds to about 0.02% of sodium chloride.

Press juice from lean meat furnishes, possibly, the nearest approach to this in composition. In respect to mineral matters, and especially with reference to potassium and phosphoric acid the pancreas juice and the muscle juice appear to be much alike. But we have here a far higher amount of protein and other organic substances. It is of course possible that beside the protein nitrogen this element may be present in some other form, in a protein derivative, as a nucleic acid, for example. But this point we have not investigated.

It is evident that the inorganic salts present are essentially phosphates of potassium and sodium, with small amounts of calcium and magnesium phosphates. There are no very exact data in the literature from which the phosphoric acid held in other forms may be calculated, but it may be assumed that a portion of the soluble protein in the juice is the α -proteid of Hammarsten. This point we have looked into. It is not likely that a lecithin body is found in the juice, because it is perfectly clear and the lecithins go with the fat fraction in the centrifugal separation.

We have identified the α -proteid¹ in a number of tests and have made some effort to estimate the amount in the press juice. The phosphorus content of the body is about 1.7%. On boiling a solution containing this protein it breaks up, splitting off a fraction called by Hammarsten β -proteid which contains about 4.5% of phosphorus. This fraction has been purified and analyzed by several chemists. Steudel found as a mean of several trials on different fractions² 4.74% of phosphorus in the substance which yields guanylic acid on splitting. In some of this work as much as 2% of the weight of the organ was secured as α -proteid, but in our preparations it is not likely that a correspondingly complete extraction was secured, but the protein which passed into solution was rich in phosphorus and acid in character.

By boiling this liquid, as in the separation of the β -proteid, we obtain a coagulum which is possibly split off from the original soluble protein. By estimating the nitrogen in this and in the filtrate we find that the 2.1% of total nitrogen is divided between 0.23% in the coagulum and 1.87% in the soluble portion. If all of this nitrogen were assumed to exist in the form of α -proteid the phosphorus corresponding would be very much below what we find in the analysis given above, suggesting that the larger part of the phosphorus must exist in some other combination. Some of the organic phosphorus bodies are possibly of acid character.

We have attempted to separate the protein bodies holding the phos-

¹ Hammarsten, *Z. physiol. Chem.*, 19, 19 (1894); Baing, *Ibid.*, 26, 133 (1898); Steudel, *Ibid.*, 53, 539 (1907).

² *Loc. cit.* and *Ibid.*, 68, 40.

phorus and roughly determine the amount of each. For the separation of the α -proteid we extracted a kilogram of minced beef pancreas with physiological salt solution at a low temperature, repeating the process a number of times. The liquids obtained were mixed and precipitated by weak acetic acid, as recommended by Hammarsten and his co-workers. The weight of precipitate obtained was considerably below what was expected from the accounts in the literature, but this may be due in part to the rather marked solubility in the wash water. In order to remove the last traces of acetic acid and to avoid putrefactive changes the last washings were made with water saturated with toluene. Something will be said below of the acid behavior of the so-prepared protein body. In appearance and general behavior our product corresponds closely to the substance described by Hammarsten and others. From our own results and those just cited it appears that vigorous extraction with salt solution will yield the α -protein in amount about 1.5% of the weight of the original moist organ. The PO_4 content corresponding is about 0.077% of the weight of the organ, and this probably represents the larger part of the α -proteid phosphorus in the whole moist organ.

Our centrifugal extraction is far from complete with respect to the total phosphorus. In one experiment with 375 g. of moist pancreas we secured 0.627 g. of P_2O_5 in the top layer, 0.888 g. of P_2O_5 in the liquid layer, and 1.128 g. of P_2O_5 in the lower layer, *exclusive* of the phosphorus found in the fat of the upper and lower layers. This makes 0.705% of P_2O_5 for the whole organ, or 0.943% as PO_4 , an amount not very different from what we secured in our composite liquid. This is a further suggestion that the α -proteid phosphorus must make up but a small part of the whole phosphorus.

It has been stated that the α -proteid gives rise to the β -proteid on decomposition and that the phosphorus can be most accurately estimated in the latter. That the larger part of the phosphorus combined with soluble protein is held in this form is suggested by another test independent of those made on the composite liquid. In this case 130 cc. of liquid were secured from a mass of minced pancreas representing about 5 kg. of the fresh organs, the weight centrifuged being about 600 g. 50 cc. of this liquid, weighing 53.2 g., furnished 9.705 g. of dry solids, or 18.24%. 75 cc. of the liquid were mixed with an equal volume of water and heated to boiling. A marked precipitate was formed which was well washed, dried and weighed. The weight was 2.25 g. equivalent to 2.82% of the weight of the liquid or 15.4% of the weight of the solids. The phosphorus content of this residue was 0.61%, as P_2O_5 , and this must represent the phosphorus split off from the α -proteid in making the β -proteid.

The filtrate from this coagulum was evaporated to dryness and tested for phosphorus, yielding 5.13% of the dry weight of P_2O_5 , a part of which

is inorganic phosphorus, and a part protein phosphorus. These determinations may be condensed as follows:

PO ₄ in total solids.....	5.990%	PO ₄ of coagulum as part of liquid..	0.023%
PO ₄ as part of whole liquid.	1.093	PO ₄ in dried filtrate from coagulum.	6.86
PO ₄ in dry coagulum.....	0.82	PO ₄ of filtrate as part of liquid.....	1.058

These results are slightly different from those of the large composite sample. The solids are somewhat higher and we have found the solids of the coagulum higher. The difference is probably due to the fact that here in the centrifugal action the temperature was permitted to run higher than was the case before, where it was kept down low enough to prevent any change in the ferments of the liquid. Elevated temperature favors a somewhat more perfect extraction. But the results are alike in showing that the larger part of the phosphorus is in the soluble fraction, that is in the fraction holding the β -proteid as well as the inorganic salts.

In several portions of this filtrate an attempt was made to throw down the β -proteid so as to secure a separation of the nuclein phosphorus from the inorganic. This was done by precipitating the liquid with dilute acetic acid and alcohol as described in the papers of Hammarsten¹ and Steudel.¹ The precipitation is not strictly quantitative, but a close approximation is reached. The determination of phosphorus in this precipitated β -proteid gives an amount of PO₄ equal to 0.037% of the liquid weight, as against 1.056% not thrown down. Different trials give essentially the same result, from which we conclude that the larger figure must represent the portion of the phosphorus not combined as a nuclein but combined in the inorganic form in the press juice.

Going back now to the composite liquid from which the larger table was made, we found, after separating a coagulum, and treating the filtrate with acetic acid and alcohol, an amount of phosphorus in the precipitate which, as PO₄ is equal to 0.023% of the weight of the original liquid. The coagulum formed by boiling in this case contained PO₄ equivalent to 0.0045% of the original liquid. The PO₄ in both amounted to 0.027% of the weight of the original liquid, from which it appears that the organic phosphorus must be very low, or, in other words, that the combination of this element is largely with metals.

This being the case will the acid and base content, as exhibited by the table, account for the reaction of the liquid? Probably not. If we combine the calcium and magnesium with phosphoric acid to form salts of the CaHPO₄ type, and the chlorine with sodium, we have left 0.841 PO₄ and sodium and potassium equivalent to 0.520 K. Taking out, further, the phosphoric acid which seems to be held in protein combination, we have remaining 0.814 PO₄ to be combined with alkalis. Cal-

¹ *Loc. cit.*

culation shows that these amounts of acid and alkali are sufficient to form a salt of the type KH_2PO_4 holding 148 parts of potassium, and a salt of the type K_2HPO_4 holding 372 parts of potassium or its equivalent, which proportions correspond closely to 4 molecules of KH_2PO_4 and 5 molecules of K_2HPO_4 . A mixture in these proportions would be slightly acid, but not as strongly acid as the potential measurements indicate.

It remains now to test the behavior of the α - and β -proteids with respect to reaction. Our various preparations of the latter compound yielded amounts of phosphorus between 4.79% and 4.94%, with nitrogen varying from 17.20 to 17.58%. Hammarsten gave 4.48%, and Steudel, in a number of preparations, found between 4.45 and 4.86% of phosphorus, with nitrogen in about the range we found. It is evident then that we are dealing with the same preparation, which is known to have an acid behavior and which breaks up easily, yielding about half its weight of guanylic acid. A solution was made of one of our preparations containing 250 mg. in 100 cc. of pure neutral 0.2 N KCl. The potential value at 20° was found to be $\pi = 0.6754$, from which $P_H = 5.797$. This value is not greatly different from those we found in the centrifugal liquids.

We have made this determination on the β -proteid because it is obtainable in a relatively pure condition. The α -proteid is more likely to be the phosphorus-holding complex in the centrifugal juice and we have therefore examined this product also, although it cannot be as readily secured in pure form. Following the methods already referred to we have made a number of preparations which are clearly acid in behavior. Great care must be taken to wash out all the acetic acid used in the precipitation of the substance from the extractive liquid, which was in some cases physiological salt solution and sometimes a stronger salt solution. It is possible that in the organ juice the α -proteid exists in combination with part of the alkali metals, rather than in the free state. Several reactions strongly suggest this, but in our calculations above we have assumed that the alkali is combined with phosphoric acid. If held with the protein the effect would be to leave the reaction of the phosphates more strongly acid. Gamgee and Jones¹ have given some experiments on this protein and suggest that it acts as a dibasic acid which yields an acid ammonium salt soluble in water. For the purpose of measuring the optical rotation of the substance they dissolved it in water plus a small amount of ammonia. They recognize in the α -proteid a body of distinctly acid character.

At any rate, by the addition of the dilute acetic acid the protein acid is set free and thrown down as a flocculent precipitate which may be washed by decantation rather easily, using toluene to prevent decomposition. It is finally washed on a filter in the same way. A little calcula-

¹ *Beit. Chem. Phys. Path.*, 4, 10 (1904).

tion shows that the acetic acid can soon be reduced to a dilution where it will give no measurable reaction in the concentration cell.

The α -proteid does not appear to be as soluble in weak potassium chloride solution as was the other product. For our tests we shook up small portions with the chloride and obtained solutions which showed a marked acid behavior in the cell. But the concentration of the solutions was always low. The acid character of the preparation is better shown in another way. We found that it dissolves in solutions of secondary sodium phosphate readily, about as it does in weak soda solution or ammonia. If this solution follows by reason of the formation of a salt at the expense of part of the sodium of the phosphate a mixture of primary and secondary phosphates would be left and the fact would be shown by an altered potential value in the cell. Our experiments confirmed this view.

We dissolved an amount of the moist α -proteid equivalent to 0.78 g. of the dry substance in 15 cc. of molar/15 Na_2HPO_4 plus 20 cc. of water (including the water held in the moist precipitate), and found for the solution at 20° a value of $\pi = 0.7330$, from which $P_H = 6.788$, or $C_H = 1.63 \times 10^{-7}$. Fifteen cc. of the same phosphate solution plus 20 cc. of water gives a mixture from which $P_H = 8.982$ was found, or $C_H = 1.03 \times 10^{-9}$. The phosphate solution has become strikingly more acid after being mixed with the protein and the final solution has about the P_H value of a mixture of 4.5 volumes of molar/15 secondary phosphate and 5.5 volumes of the corresponding primary phosphate. This change corresponds to the removal of a certain amount of sodium from the secondary phosphate solution, and practically the equivalent of 0.842 g. per liter, or 12.6 mg. for the 15 cc. used in dissolving the protein.

It is evident, therefore, that this so-called α -proteid is a distinctly acid substance. In our centrifugal juice it may act as an acid or it may hold part of the sodium in salt form. Probably the latter is the true condition, and the original combination in the organ must be an alkali salt of the nucleoproteins present. The effect of this would be to leave more of the phosphorus combined as a primary phosphate and increase the acidity of the press juice. It must be recalled that besides the α -proteid the pancreas is known to contain other similar bodies which are not readily separated from the solvent liquid. If these have the same markedly acid character as this one, we have a further explanation of the acid reaction of the organ.

We wish to acknowledge in this place our indebtedness to Mr. R. A. Nelson and Miss Mary Hull for valuable help in the preparation of material and in the analysis of solutions described.

Summary.

1. We have shown by a large number of qualitative experiments on individual organs of freshly slaughtered animals that the normal reac-

tion of the pancreas is distinctly acid. This confirms and extends the conclusions of our former paper regarding the pancreases of the hog, beef and sheep.

2. The quantitative relations were studied on organs collected from September to December to cover possible seasonal or feeding variations, and results were found which show that the reactions of the pancreases of the three animals are essentially as reported before, with the P_H values running between 5.5 and 5.7. There appears to be no seasonal effect, and the condition of the animal was evidently without influence. This ion concentration is then nearly a constant and is undoubtedly a factor of physiological importance.

3. Similar experiments were made on the organs of other animals. It was found that the parotid glands, the liver and the spleen were acid in reaction, but not to the extent found for the pancreas, while the bile was slightly alkaline or neutral and the thyroid gland practically neutral, as might be expected from the location and relations of the gland.

4. In searching for the cause of the reaction of the pancreas a complete analysis of the salts of the press juice was made. The juice is rich in phosphates, while sulfates are absent and chlorides present only in traces. Of the metals, potassium is the most abundant and the relations of all the metals to the phosphoric acid is such as to give rise to a slightly acid reaction.

5. In addition to this reaction of the inorganic salts it is found that the nucleoproteins present have an acid reaction, and that one of them, at least, the α -proteid of Hammarsten, goes readily into solution with secondary sodium phosphate, in which solution the reaction of the phosphate changes from alkaline to acid, apparently from the formation of primary phosphate.

6. It appears that the marked acid reaction of the pancreas, which is stronger than found for other organs, may be accounted for through the presence of acid phosphates and acid nucleoproteins. The alkali salts of the nucleoproteins are readily soluble in water and therefore pass into the centrifugal or press juice.

CHICAGO, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN.]

THE INFLUENCE OF SOME SOLVENTS ON THE RATE OF ACTION OF SODIUM WITH ISOAMYL BROMIDE.

By PAUL WHITTIER CARLETON.

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Three types of solvents, ether, tertiary amines, and hydrocarbons, have particular interest because of their relation to the formation of the

Grignard reagent. In ether and tertiary amines this reagent forms by the action of magnesium on the organic haloid. A hydrocarbon solution of the haloid is not thus acted upon at ordinary temperatures. Tschelinzeff¹ has found that small amounts of ether or tertiary amine in the hydrocarbon solution cause the formation of the reagent at a lower temperature. The catalytic action² of the ether or tertiary amine he explained by the dissociating effect of these substances on the organic haloids.

It was considered of interest to see whether an alkyl haloid in ether solution would react with sodium faster than when dissolved in benzene. With this in mind, attempts were made to obtain comparative measurements for the rates of reaction between sodium and isoamylbromide when the latter was dissolved to a 0.1 *N* solution in ether, in benzene, and in dimethyl aniline.

Purification of Reagents.—The ether was shaken out with water three times, dried with fused calcium chloride, then with finely divided sodium and was finally distilled from phosphorus pentoxide. It was kept in the dark with sodium. The benzene was shaken with concentrated sulfuric acid several times, with sodium hydroxide solution and then with water. It was dried with fused calcium chloride and then finely divided sodium, was refluxed and distilled from sodium. It was kept in the dark with sodium in it. The dimethyl aniline was dried with sodium and distilled. The xylene was boiled with sodium, the gasoline was shaken out with concentrated sulfuric acid, and fractionated. The hydrogen was passed through water, sulfuric acid, phosphorus pentoxide, and sodium.

Plan of Experiment.—Twenty cc. of 0.1 *N* isoamylbromide solution were shaken for a definite length of time with a large excess of finely divided sodium in a stoppered flask in a thermostat. The flask was then opened and the sodium was filtered off, washed with pure solvent and then treated with alcohol. The alcoholic solution was diluted and after proper treatment titrated to determine the amount of sodium bromide formed. This gave in cc. 0.1 *N* silver nitrate solution a measure of the amount of isoamylbromide which had reacted in any way with sodium.

Apparatus.—The shaker was a piece of two-inch plank made to carry four samples. It had two holes on each side in which the necks of the flasks fitted, being held in place by wooden clips. This plank was pushed back and fourth on the surface of the water in the thermostat. The bulb of the flask was immersed, leaving only the top of the neck exposed. The shaking was efficient as could be seen by the distribution of the sodium over the inside of the flask. The temperature of the thermostat was 25°.

¹ *Ber.*, 37, 4537-4538 (1904).

² Stadnikoff (*J. prakt. Chem.*, [3] 88, 1 (1913)) denies this role for the ether. See in reply Tschelinzeff (*J. prakt. Chem.*, [3] 89, 86 (1914)).

Experimental.

The sodium (5 or 7.5 g. weighed to 0.01 g.) was melted under boiling xylene in the flask in which the reaction was to take place, which was a 100 cc. round bottom, long-necked, Jena flask. The flask was stoppered and shaken vigorously, then opened and cold xylene poured in. This method, a modified suggestion of Brühl,¹ gave the metal in a finely divided condition. The particles in any one sample were not uniform in size, but the different samples were very similar even upon close examination. The flask containing the xylene and finely divided sodium was attached to an apparatus so arranged that it could be filled with dry hydrogen, or that diminished pressure could be maintained by a water pump. It was also possible, without admitting air, to draw a liquid first into the flask to rinse it and then into a catch bottle. Hydrogen was used when necessary to increase the pressure within the system. A sulfuric acid wash bottle just before the pump kept out moisture from this source. When the flask was first connected with this apparatus the air in it was replaced by hydrogen and the xylene was drawn over into the catch bottle. The sodium was washed twice with gasoline boiling below 75° and once with petroleum ether boiling below 50°. After most of this had been removed, the small amount remaining was evaporated under diminished pressure by immersing the flask in hot water. The flask was several times alternately filled with hydrogen and evacuated to get rid of traces of hydrocarbon. In this way sodium was washed free from xylene in an atmosphere of hydrogen and was finally obtained perfectly dry in a finely divided condition with a bright metallic surface. There was usually present a trace of sodium hydroxide formed during weighing. Hydrogen was then admitted to the full pressure of the generator and the sodium was ready for use.

The average size of the sodium particles was not greater than 0.1 to 0.2 mm. in diameter, and in no case were there any particles larger than 1 mm. It did not seem practicable to try to obtain more uniform material than this, since so large an excess of sodium was used (100 to 150 atoms).

The surface exposed is an important factor in a heterogeneous reaction. The large amount of sodium was chosen to make the surface relatively enormous, 7.5 g. of sodium in spheres having a diameter of 0.3 mm. would have a surface of over 1500 sq. cm. The actual surface exposed could not have been smaller, as the average diameter must have been less than 0.3 mm. The particles were compared with a scale ruled in millimeters in order to know their approximate size. This surface (1500 sq. cm. for 7.5 g. or 1000 sq. cm. for 5 g.) was available for reaction with 20 cc. 0.1 *N* solution of isoamylbromide (0.302 g.).

¹ *Ber.*, 35, 3516 (1902), footnote.

In order to reduce the evaporation on pouring the ether solution into the buret, the volumetric flask was closed with a two-holed rubber stopper carrying a long and a short piece of glass tubing. On inverting the flask, ether flowed out the short tube into the buret, while air entered the flask through the long tube without bubbling through the solution.

For measuring the isoamylbromide solution a buret was used which was drawn out to a long capillary below the glass stopcock. This capillary entered the flask through a glass tube in the stopper and extended almost down to the sodium. Twenty cc. of the 0.1 *N* isoamylbromide were added, and the flask was withdrawn from the rubber stopper, closed by a solid rubber stopper and shaken in the thermostat.

The reaction was stopped by filtering the sodium and washing it three times with the solvent, except in the case of dimethyl aniline. When this was used as the solvent, if sufficient time were allowed for the reaction, there was present a whitish flocculent suspension. On exposure to air, this was rapidly discolored to a brown slime which hindered filtration very much, even when suction was used. It was necessary to remove the dimethyl aniline as completely as possible, because of the color which even small amounts of it caused in the solution during titration. The final method was to dilute with gasoline before filtering off the sodium, then filter and wash with gasoline. Even with this modification, however, special treatment was necessary before the bromide could be titrated.

The sodium from benzene or ether experiments was treated with alcohol, the flask and filter were washed into this solution with water, and the solution was diluted, acidified with nitric acid, and titrated according to the Volhard method. A few of the solutions, after being exactly neutralized with 0.5 *N* nitric acid, were titrated, using potassium chromate as indicator.

The procedure when dimethyl aniline had been used was as follows: The sodium alcoholate was neutralized by cold alcoholic nitric acid, the solution filtered, and the filtrate evaporated to dryness, leaving a dark residue. This was triturated with pure benzene to dissolve the colored substance which was filtered off. The sodium bromide obtained by both procedures was dissolved in water and titrated according to the Mohr method. In the earlier cases, titrated by the Volhard method because of the color caused by traces of dimethyl aniline, it was necessary to approach the end point several times from each direction and take the average of these as correct.

The results in Table I fairly represent those obtained. In the case of the ether solution the figures given include all of the results from the last solution used, with those for 30, 72 and 96 hours from a previous solution. 7.5 g. of sodium were used in all of the experiments with ether save the last three where 5 g. were used. All of the data obtained using

dimethyl aniline and benzene as solvents are not included, as they merely emphasize the results given in the table. With benzene and dimethyl aniline solutions 5 g. of sodium were used save in the last two experiments with dimethyl aniline where 7.5 g. were used. A large number of experiments were made with ether as the solvent, in some of which 7.5 g. of sodium were used, in others 5 g., but no difference in results due to this change could be detected. The results are expressed in cc. of 0.1 *N* silver nitrate required to titrate the sodium bromide formed. Isoamyl-bromide was dissolved to 0.1 *N* solution in these solvents. The time is expressed in hours.

TABLE I.

Cc. of 0.1 *N* AgNO₃ required for NaBr formed from C₆H₁₁Br in solvents named.

Time, (hours).	Solvents.				Time, (hours).	Solvents.	
	Ether.		Dimethylaniline.	Benzene.		Ether.	Benzene.
1	0.9	1.0	18.7	0.5	18	1.0
2	0.7	1.0	18.2	0.7	30	15.0	...
3	0.6	2.0	0.95 18.6	0.8	47	0.8
4	7.1 ¹	0.8	18.6	0.8	72	18.9	...
5	1.1 (B) ²	21.2 ¹	96	20.4	...
6	1.5	3.1	20.6	0.8	358	1.9

These results show that the reaction in benzene does not complete itself within a reasonable length of time. In ether the reaction goes to completion within four days, while in dimethylaniline it is complete in a few hours. The solubilities concerned are not known.

That the rates of reaction do not bear any simple relation to the dielectric constants of the solvents is not surprising, since different reactions take place. In dimethylaniline the ammonium salt (dimethyl isoamyl phenylammonium bromide) is formed and sodium reacts with it as a positive metal replacing a less positive radical.²

A similar sort of reaction is possible also with the ether solution, but must be a minor reaction, as the formation of the oxonium salt is very slight. This kind of reaction is not possible in benzene solution.

As stated before, Table I does not give all the results. Many attempts were made, especially with ether solutions, to find the cause for the lack of agreement. It was the intention to obtain comparable results, and as far as the appearance of the sodium was concerned, this seemed to be accomplished. Uniform results were not obtained even with improvements in apparatus and technic. An unsuccessful attempt was made

¹ The sodium in these cases seemed more oxidized. Although in the case of (B) 21.2 cc. air was admitted by mistake, it could hardly have caused this deviation. See the later air experiments. The excess of 1.2 cc. in (B) is due to 21 cc. of 0.1 *N* C₆H₁₁Br being used by mistake.

² See E. E. Blaise, *Bull. soc. chim.*, [3] 35, 93 (1906), and Grignard, *Ibid.*, [4] 1, 260 (1907), who found tetraalkyl ammonium iodides did not react with magnesium.

to connect this lack of agreement with the effect of light by noting whether the day was cloudy or clear. This was thought of, since the trials started at any one time agreed, while those of different days did not. It has been stated that no difference in results was detected when 7.5 g. of sodium were used in place of 5 g., hence the comparatively small variation in amount of surface exposed could have had no marked effect.

The reaction resulting in the formation of sodium bromide did not uniformly attack the whole surface of the metal. The blue form of sodium bromide, which was not noticeable until equivalent to about 4 cc. of 0.1 *N* silver nitrate, was present as little blue balls scattered throughout the mass; the rest of the metal was not visibly changed. It was suspected that these particular bits of sodium might have been oxidized to sodium hydroxide, but the experiments with moist air and moist ether described later did not justify this. When a trace of alcohol was added, the blue was uniformly distributed over the whole surface.

The difficulty cannot be due to halogen in the sodium, since several blanks using large weights of substance showed none. What should cause such a result as total reaction in five hours in ether solution (B) in Table I is not known.

In order to find the effect of air and other gases on the rate of reaction, the following experiments were tried, using 0.1 *N* ether solution of isoamylbromide. The results are expressed as cc. of 0.1 *N* silver nitrate required to titrate the sodium bromide formed.

TABLE II.
The effect of enclosed gas.

Time (hours).	Cc. 0.1 <i>N</i> AgNO ₃ .	Enclosed gas.
3	0.95	Hydrogen (as usual).
3	1.0	Air-dried by H ₂ SO ₄ passed through about a minute.
3	1.5	Undried air, same length of time.
3	1.4	Dried carbon dioxide, same length of time.

Although there are small variations here, the differences are not such as were obtained in the regular series. The following data show the variations in the results for three hours—all the data for this length of time with ether solution are given here (expressed as cc. of 0.1 *N* silver nitrate solution).

TABLE III.
The results are arranged in chronological order.

						g. Na.
Solution A....	3.4					7.5
Solution B....	1.5	0.9				5.0
Solution C....	0.4	0.45	2.2	4.2	1.0	5.0
Solution D....	0.6	2.0	0.95			7.5

TABLE IV.
Effect of moisture and alcohol when benzene is solvent.

Wt. of sodium.	Time, (hrs.).	Cc. 0.1 N AgNO ₃ required.	Impurity.
7.5	2	3.7	0.1 cc. alcohol in 1 cc. benzene.
7.5	2	2.7	1 cc. benzene satd. water.
7.5	2	0.7	None.

The sodium used in the first two trials given with Solution C had stood in hydrogen five days dry in powder form.

That the air admitted in quickly withdrawing one stopper and inserting another would not seriously affect the results, is shown by Table II. These data also eliminate the variation in the surface of the sodium as a determining factor in variation of results.

Another factor, moisture, was investigated as follows: 5 g. of sodium with 20 cc. of 0.1 N ether solution of isoamylbromide and 0.1 cc. of ether saturated with water after shaking three hours required, after the usual treatment, 1.1 cc. 0.1 N silver nitrate for the sodium bromide present. In another case 7.5 g. of sodium with similar solutions except that 1 cc. of wet ether was used and the mixture was shaken two hours, required 1.1 cc. 0.1 N silver nitrate. These trials were carried out four months apart with different solutions and different preparations of reagents. They show that moisture has no accelerating effect on the reaction, perhaps a surprising fact, and eliminate the presence of the sodium hydroxide as the disturbing agent.

When benzene was the solvent, moisture increased the speed of reaction. 7.5 g. of sodium were shaken for two hours with 20 cc. of 0.1 N benzene solution of C₅H₁₁Br plus 1 cc. of benzene saturated with water and sodium bromide equivalent to 2.7 cc. 0.1 N AgNO₃ was formed. This is a greater value than any with dry benzene.

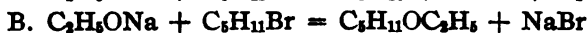
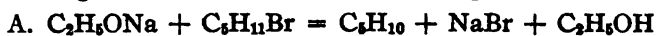
The influence of small amounts of other impurities on the speed of reaction (as indicated by the sodium bromide) was studied. The experiments are given with the blank run at the same time for the reason, previously stated, that trials made at the same time usually gave concordant results. In the following table the weight of sodium given was shaken with 20 cc. of 0.1 N ether solution of isoamylbromide plus 0.1 cc. of ether containing the amount of impurity stated. The sodium bromide formed required the volume of 0.1 N AgNO₃ solution given.

Part A of the table shows that the impurities there introduced have no marked effect in the three hours which the reaction is allowed to go. That the reaction is slower is noticeable in Part B. The impurities used in C have also no decided influence. Alcohol and acetone in Part D cause the reactions to go to completion in three hours. This is not unexpected, but these experiments show very clearly the importance of freeing the ether from the last traces of alcohol for uses of this kind.

0.01 cc. of alcohol corresponds to 0.05% alcohol in the ether, and with this purity the reaction goes 85% in two hours and 100% in three hours. With pure ether the reaction has gone about 5% in two and 10% in three hours.

The acceleration caused by alcohol is, of course, due to the fact that different reactions are taking place. Sodium with alcohol forms sodium ethylate, which reacts with the alkyl bromide. The sum of reactions involving sodium ethylate as well as metallic sodium is being measured.

The following additional reactions then take place:



Reaction A is much faster than that of sodium on the alkyl haloid. The data in Table V do not indicate how much faster Reaction A is, for the total amount of alcohol is less than one-tenth of a molecule compared to the alkyl bromide, and yet although both Reactions A and B are taking place, only A regenerates alcohol to form more sodium ethylate and react with more alkyl bromide, thus finally yielding sodium bromide equivalent to all of the isoamylbromide present. In the ether filtrate from the sodium and sodium bromide, when 0.01 cc. of alcohol had been added before the reaction, unsaturation was detected by the disappearance of bromine color, while the color in the blank remained. In another case where no alcohol had been used, unsaturation was not detected.

The effect of alcohol when benzene was the solvent was tested. 7.5 g. of sodium powder were shaken with 20 cc. of 0.1 N benzene solution of isoamylbromide and the impurity stated.

TABLE V.

The effect of some impurities.

Grams of sodium.	Time in hours.	Cc. 0.1 N AgNO ₃ required.	Impurity.	Grams of sodium.	Time in hours.	Cc. 0.1 N AgNO ₃ required.	Impurity.
Series A:				Series D:			
5	3	3.6	0.01 cc. benzene (dry)	5	3	22.2	0.01 cc. abs. alcohol
5	3	3.3	0.01 cc. xylene (dry)	5	3	22.3	0.01 cc. anhyd. acetone
5	3	4.0	0.05 cc. pentane	5	3	4.4	0.01 cc. ethyl acetate, dry, alcohol free
5	3	4.2	Blank	5	3	2.2	Blank
Series B:				Series E:			
5	10	0.95	0.01 cc. benzene (dry)	7.5	2	21.0	1 cc. ether contg. 0.1 cc. abs. alcohol
5	10	2.25	Blank	7.5	2	16.8	0.1 cc. ether contg. 0.01 cc. abs. alcohol
Series C:							
5	3	1.05	0.1 cc. ether satd. water				
5	3	0.85	0.01 cc. acetoacetic ester				
5	3	1.16	0.01 cc. malonic ester				
5	3	1.0	Blank				

These results, when compared with those obtained in using an ether solution, show clearly that the sodium ethylate reactions with the alkyl haloid also go much slower in benzene solution.

Summary.

1. An attempt has been made to measure the rate of reaction of metallic sodium in powder form with isoamylbromide dissolved in ether, in dimethylaniline and in benzene.
2. The rate in ether was faster than in benzene, while in dimethylaniline the rate was much greater than in either of the other two.
3. This can be explained by the formation of ammonium and oxonium (very slight) salts and by the sodium replacing the less positive organic basic radical in the salt. It cannot be explained if dissociation of the alkyl haloid alone is used and if the dissociating power of a solvent is proportional to its dielectric constant.
4. Chemically this result would be expected, as the dimethylaniline would certainly add the haloid and the ether would tend to do so, while benzene would not.
5. The effect of some impurities on the rate of reaction has been shown. That of alcohol and acetone is enormous.

MADISON, WIS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA.]

THE DETERMINATION OF ACETONE IN SYSTEMS OF METHYL ALCOHOL, WATER AND POTASSIUM FLUORIDE, AND EQUILIBRIA IN SYSTEMS OF METHYL ETHYL KETONE, WATER AND INORGANIC SALTS.

By G. B. FRANKFORTER AND LILLIAN COHEN.

Received March 13, 1916.

In the study of the equilibria in the systems water, acetone and inorganic salts, it was found that the amount of acetone present in an aqueous solution can be determined. It was also found that methyl alcohol cannot be salted out of an aqueous solution by means of potassium fluoride. It was thought that acetone could be then accurately determined in the presence of methyl alcohol. When the methyl alcohol did not exceed 5%, its function was found to be the same as water, and from a study of the binodal curve, the amount of acetone in a solution could be determined. It was found, however, that when larger amounts of methyl alcohol were used the alcohol did not act the same as the water, and loci of points found by experiment did not fall on the binodal curve. A more or less comprehensive study of the effect of the alcohol was then made. Solutions containing from 5-95% methyl alcohol in water were made up and the salting out effect of potassium fluoride was again tried. The

method used is the same as the one described,¹ only in this case the alcohol and water mixtures were used in place of water.

If a careful study is made of Table I, it will be seen that it does not seem to be the amount of methyl alcohol, but rather the amount of acetone that gives discordant results. When the percentage of acetone does not exceed 18, the acetone can be determined as in the method described. If the amount of acetone present exceeds 18% the solution must be diluted and the acetone can then be determined, the methyl alcohol not interfering in this determination.

TABLE I.

1. KF.	2. Water.	3. Methyl alcohol.	4. Acetone.	5. Acetone.	6. Water.
17.65	29.80	44.70	7.85	8.00	74.50
16.35	51.28	21.97	10.40	10.00	74.00
15.91	59.89	14.97	9.23	9.50	74.00
14.57	44.59	29.73	11.11	11.50	74.00
13.75	43.48	28.98	13.79	13.50	73.50
10.67	42.60	28.40	18.33	18.00	70.50
9.75	48.57	20.81	20.87	24.00	66.50
9.29	28.54	42.80	19.37	25.00	66.00
8.92	35.15	35.15	20.78	25.00	66.00
7.33	40.17	26.77	25.73	29.50	63.00
7.02	43.06	10.76	39.16	31.00	62.00
7.62	28.02	42.04	22.32	29.50	63.00
5.78	42.30	10.57	41.35	37.00	58.00
5.30	32.53	32.53	29.64	37.00	58.00
5.16	26.35	39.53	28.96	39.00	56.00
4.97	41.10	10.27	43.66	40.00	55.00
5.19	37.91	25.28	31.62	39.00	56.00
4.21	39.83	9.96	46.00	44.00	52.00
4.12	40.96	17.54	37.38	45.00	51.00
4.46	31.28	31.28	32.98	42.00	54.00
4.05	24.83	37.25	33.87	45.00	51.00
3.99	35.90	23.93	36.18	45.00	51.00
3.82	14.72	44.16	37.31	47.00	50.00
3.65	30.14	30.14	36.08	47.00	49.00
3.37	39.20	16.80	40.63	50.00	47.00
3.10	23.59	35.38	37.93	50.00	47.00
3.03	33.97	22.65	40.35	50.00	47.00
2.75	28.00	28.00	41.25	52.00	46.00
2.43	36.20	15.52	45.85	52.00	46.00
2.42	35.82	8.96	52.80	52.00	46.00
2.10	25.79	25.79	46.32	54.00	44.00
1.93	34.22	8.55	55.30	58.00	41.00
1.72	11.30	33.92	53.06	58.00	41.00

In the table, Columns 1, 2, 3, 4, respectively, indicate the weight in grams of KF, water, alcohol and acetone in 100 g. of the solution. Columns 5 and 6 show the weight of acetone and water, respectively, in grams

¹ THIS JOURNAL, 36, 1103-34 (1914).

that should be present in 100 g. of the solution, if no methyl alcohol were present. The data from 5 and 6 were found in a former experiment.¹ The data in 1, 2, 3, 4 are those just determined.

Equilibria in Methyl Ethyl Ketone Systems.—The methyl ethyl ketone which was used in the following experiments came from the firm of C. A. F. Kahlbaum, of Berlin, and was labelled highest purity. An examination showed, however, that it was by no means pure, although of better quality than a sample of the same supposed purity from another factory. The Kahlbaum sample began to boil at 78° and rose to 84° before it had all distilled over. After fractioning several times, that part which passed over between 79.5° and 80.5° was collected and treated with magnesium, amalgam and finally with metallic sodium. It was again fractioned, practically all passing over between 79.6–80.2° at 745 mm. pressure. The purified sample was then weighed. It represented about 60% of the total sample taken; the remaining 40% included impurities and loss sustained in the purification. It was again redistilled, a very small amount passing over below 80°. The remaining part distilled at 80 to 80.2 at 752 mm. The specific gravity was taken at 20° in a specially designed and standardized vacuum pycnometer and gave 0.8054 and 0.8051²⁰/₄.

The refractive index was taken with the latest Pulfrich refractometer using the newly designed hydrogen tube. The average of three determinations gave the following indices:

Alpha.... 1.38308; Beta.... 1.37023; Gamma.... 1.36178

Compared with the physical constants determined by others these are in fairly close accord, as will be seen by the following table:

Sp. gr. 0.82961 at 0°; 0.8125 at 13°; 0.8045 at 19.8°; 0.80526 average of two determinations.

Boiling point 80.6; 80.6; 80–80.2°; 80–80.2.

The last numbers were taken by the authors. It will be seen that the specific gravities agree fairly well but there is a slight difference in the boiling points. As the atmospheric pressure is not given in the determinations made by others we may assume that the pressure was normal or perhaps higher than that under which we work. This could easily account for the difference. The purified sample was kept in a double stoppered bottle away from the light until it was used in the accompanying experiments.

Methyl ethyl ketone can be salted out from its aqueous solution by the salts sodium chloride, potassium fluoride and potassium carbonate. The percentage of ketone in the aqueous solution can be approximately determined by means of these salts. For accurate determinations, this method would not be satisfactory.

The systems water, methyl ethyl ketone, water and sodium chloride;


¹ *Loc. cit.*

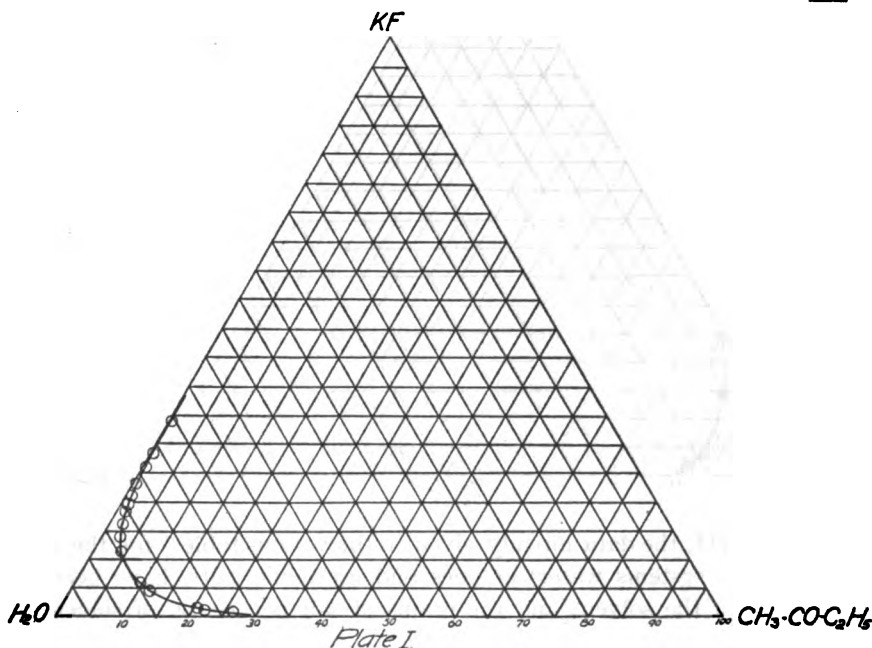
ethyl methyl ketone, water and potassium fluoride; ethyl methyl ketone, water and potassium carbonate were studied and the binodal curve for each is given. The data for the systems are given in Tables II, III and IV. The results with potassium carbonate were not satisfactory.

TABLE II.

System Potassium Fluoride, Water and Methyl Ethyl Ketone.

Total wt. of subst. present.				% in 100 g. of sol.		
KF.	Ketone.	Water.	Total.	KF.	Ketone.	Water.
10.869	0.870	45.691	57.430	18.93	1.51	79.56
10.896	5.06	87.541	103.47	10.50	4.87	84.63
10.869	5.05	87.54	103.45	10.50	4.87	84.63
10.869	19.82	160.671	190.46	5.70	9.93	84.37
1.99	6.24	42.003	50.233	3.96	12.42	83.61
0.647	16.363	60.077	77.087	0.84	21.23	77.93
0.647	46.063	148.957	195.667	0.34	23.55	76.11
47.156	1.00	151.53	199.686	23.63	0.50	75.87
47.156	1.55	170.66	219.366	21.49	0.70	77.81
29.454	0.15	56.096	85.700	34.38	0.17	65.45
29.454	2.37	126.396	158.22	18.62	1.49	79.89
29.454	4.07	151.646	185.170	15.91	2.19	81.90
29.454	6.37	177.546	213.37	13.80	2.98	83.22

In all the studies we have so far made the two liquids in the systems have been miscible in all proportions. There is a limit to the solubility of methyl ethyl ketone in water and water in ethyl methyl ketone. 

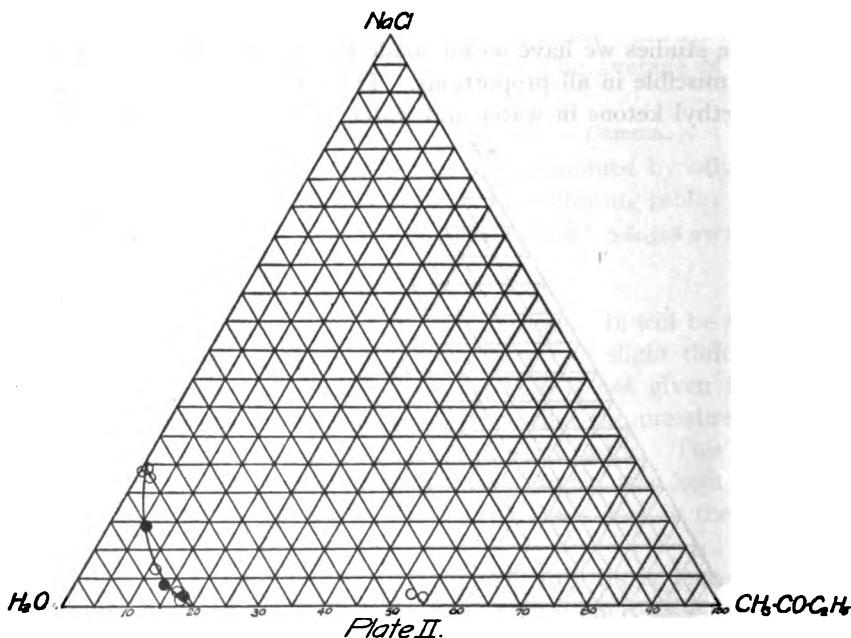


The solubility of the 2 liquids in each other is not only influenced by the temperature but also by the presence of inorganic salts. The influence of potassium fluoride is shown by Table II and Plate I. The effect of sodium chloride is shown in Plate II and Table III.

TABLE III.

System Sodium Chloride, Water and Methyl Ethyl Ketone.

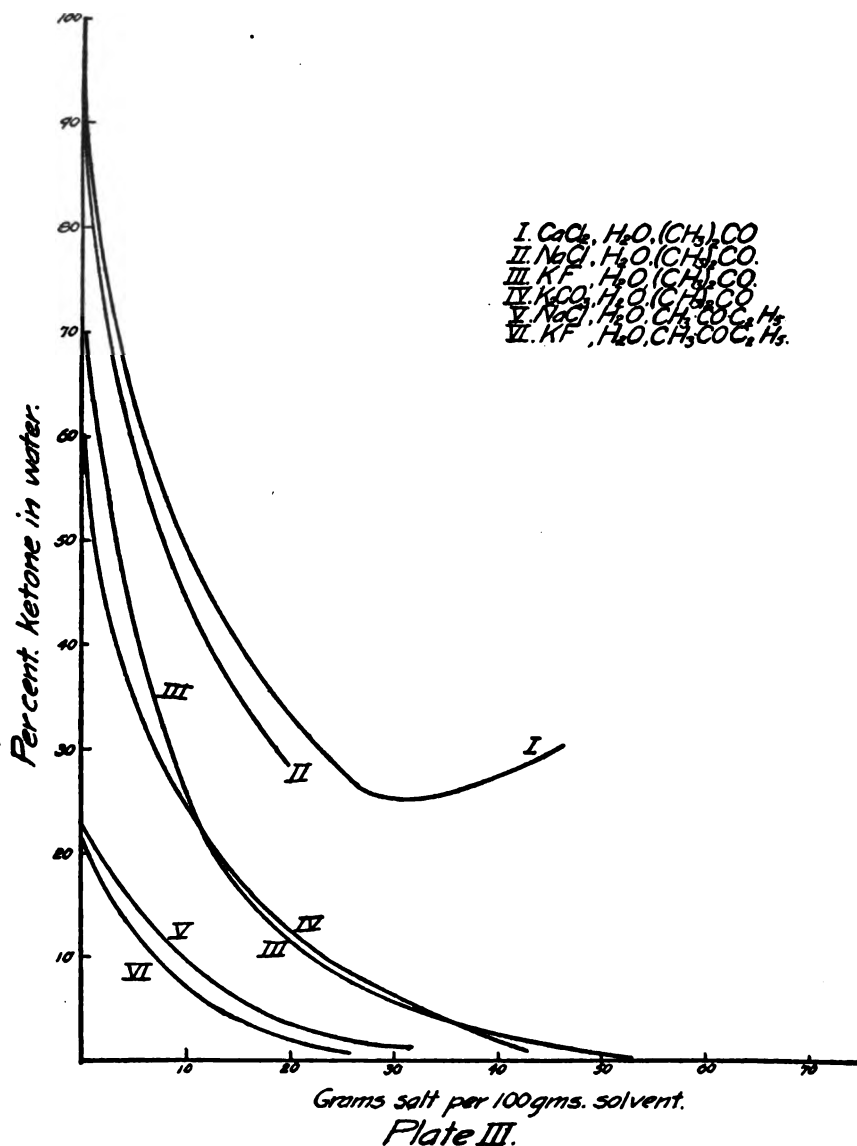
Total wt. of subst. present.				% in 100 g. of the sol.		
NaCl.	Ketone.	Water.	Total.	NaCl.	Ketone.	Water.
2.737	0.718	15.235	18.69	14.65	3.83	81.52
2.737	2.085	22.375	27.197	10.07	7.65	82.28
2.737	4.380	33.445	40.562	6.75	10.80	82.45
2.737	8.87	54.89	66.497	4.11	13.34	82.55
2.737	18.02	90.17	110.927	2.47	16.24	81.29
2.737	26.69	121.55	150.98	1.80	17.70	80.50
0.501	5.828	28.943	35.272	1.42	16.52	82.06
0.501	18.118	73.113	91.732	0.55	19.75	79.70
0.501	28.918	114.263	143.682	0.35	20.13	79.52
15.740	0.605	48.847	65.192	24.14	0.94	74.92
15.740	1.425	50.847	68.012	23.15	2.08	74.77
15.740	5.9	88.272	109.912	14.32	5.36	80.32



In Plate III, the data already given in the various tables¹ for the equilibria in the systems water, ketones and inorganic salts, have been replotted, with the solvent and the grams of salt per 100 g. of solvent as

¹ *Loc. cit.*

rectangular coördinates. The object of this was to show, if possible, the influence exerted by the acid radical on the salting out property. No



relationship is apparently indicated by these curves. That hydration has an influence is indicated by the break in the calcium chloride curve.

MINNEAPOLIS, MINN.

ORTHOBENZOYL-BENZOYL CHLORIDE.

By H. C. MARTIN.

Received March 16, 1916.

o-Benzoyl-benzoic acid has been represented by two tautomeric formulas. The necessity for this was based on the behavior of the acid chloride.

Haller and Guyot¹ prepared *o*-benzoyl-benzoyl chloride by treating the anhydrous acid with phosphorus pentachloride in carbon disulfide. Large colorless crystals were obtained melting about 70°. They sug-

gested the formula $\text{C}_6\text{H}_5 \begin{array}{l} \text{CClC}_6\text{H}_5 \\ >\text{O} \\ \text{CO} \end{array}$ because on treating the acid chloride

with benzene and aluminium chloride it gave diphenylphthalide.

Graebe and Ullman² have shown that, if, in the preparation of the acid chloride, temperatures above 100° are used, the product is anthraquinone. This would indicate the formula $\text{C}_6\text{H}_5\text{—CO—C}_6\text{H}_4\text{—COCl}$, and the preparation of the amide and the change of the latter to aminobenzophenone is in accordance with the latter formula. Haller and Guyot also prepared the methyl ester of *o*-benzoyl-benzoic acid in five different ways, including the action of the acid chloride on methyl alcohol, and in each case obtained the ester first described by Plascuda³ (m. p. 51–52°).

Meyer⁴ prepared the acid chloride of *o*-benzoyl-benzoic acid by dissolving the acid in thionyl chloride and removing the excess of thionyl chloride in a current of dry air at 50°. He obtained a colorless syrup which would not crystallize but which, when added to methyl alcohol, gave an ester having the melting point 80–81°. Meyer obtained the same ester from the acid chloride prepared by the action of phosphorus trichloride on the acid. He tried in various ways to convert this ester into the ester having the melting point 51–52° but always failed, and he concluded that the acid chloride prepared by the thionyl chloride method or by the phosphorus trichloride method is the isomeric form of that obtained by the use of phosphorus pentachloride.

The author prepared *o*-benzoyl-benzoyl chloride using the method employed by Haller and Guyot. 22.6 g. of the anhydrous acid were suspended in 300 g. of carbon disulfide and 20.8 g. of phosphorus pentachloride added in small portions. After the evolution of hydrogen chloride had ceased the carbon disulfide and phosphorus oxychloride were distilled off under reduced pressure, the temperature being kept below 100°. The thick heavy oil was dissolved in anhydrous ether and the solution, allowed to evaporate slowly over sulfuric acid, gave large colorless crystals, m. p. 59–60°. Several attempts to crystallize the oil by

¹ *Bull. soc. chim.*, [3] 25, 54 (1901).

² *Ann.*, 291, 10 (1896).

³ *Ber.*, 7, 987 (1874).

⁴ *Monatsh.*, 25, 475 (1904).

dissolving in benzene and adding ligroin proved fruitless, although this is the method described by Haller and Guyot.

The acid chloride was also prepared by Meyer's method. 15 g. of the anhydrous acid were dissolved in about 15 cc. of pure, almost colorless thionyl chloride. A current of dry air was then passed through the flask which was heated to about 50° and after a few hours the contents of the flask solidified. This was recrystallized from ether and gave crystals, m. p. 59–60°, identical with those obtained by the other method.

Through the kindness of Prof. T. L. Walker, a microscopic examination of these crystals was obtained. They are doubly refracting and biaxial, their commonest section is a rhomb and they extinguish parallel to the diagonals of the rhomb, indicating a crystal of the rhombic, monoclinic or triclinic system.

As the acid chloride is extremely easily affected by the moisture of the air, it was difficult to get a good specimen for analysis and the chlorine content came low.

Calc. for $C_{14}H_9O_2Cl$: Cl, 14.5. Found: Cl, 13.6.

Preparation of the Cyanide.—Three methods were used in the attempt to prepare *o*-benzoyl-benzoyl cyanide.

1. The acid chloride and mercuric cyanide were dissolved in anhydrous acetone and heated on the water bath for several hours.

2. The acid chloride and anhydrous hydrogen cyanide were dissolved in anhydrous ether and pyridine added.

3. The acid chloride and mercuric cyanide were heated in a sealed tube.

The third method was the only one which yielded any cyanide and it was also unsuccessful when potassium cyanide was substituted for the mercuric salt. About 10 g. of the acid chloride prepared by the thionyl chloride method was mixed with an excess of finely ground mercuric cyanide and heated 8–9 hours in a sealed tube at 155–165°. Great care must be taken to prevent exposure of the chloride to air and temperatures higher than 165° decrease the yield. The contents of the tube were treated with alcohol and filtered. On adding water to the alcohol solution it turned milky and, on standing, white crystals separated out which were further purified by redissolving in alcohol and adding water. Yield about 65%.

Calc. for $C_6H_5.CO.C_6H_4.CO.CN$: N, 5.97. Found: N, 6.09, 5.97, 5.99.

The cyanide melts at 70°, and is very soluble in acetone, ether, benzene, toluene, acetic acid and ethyl acetate; less soluble in alcohol and ligroin and insoluble in water.

This preparation was repeated, using 10 g. of the chloride prepared by the use of phosphorus pentachloride. The yield was about 50% and the cyanide was identical with that obtained in the first preparation.

Summary.

1. *o*-Benzoyl-benzoyl chloride has been prepared by the action of phosphorus pentachloride on the acid. Its m. p. is 59–60° while that obtained by previous investigators melted about 70°. Possibly their chloride had been affected by moisture.

2. *o*-Benzoyl-benzoyl chloride has also been prepared by the action of thionyl chloride on the acid. It is identical with the product obtained by the previous method. It had previously been described as a thick oil which would not solidify and was thought by Meyer to be an isomer of the other.

3. *o*-Benzoyl-benzoyl cyanide has been prepared by the action of mercuric cyanide on the acid chloride obtained by each of these methods. The same product is obtained.

4. The experiments described give no evidence of a necessity for tautomeric formulas for *o*-benzoyl-benzoic acid.

The preparation of the esters is being repeated in this laboratory and the results will be published very shortly.

These experiments were carried out under the direction of Professor F. B. Allan.

UNIVERSITY OF TORONTO.

CORRECTION.

On page 391 of the February issue read "*p*-nitrophenylhydrazone" and "*p*-nitrophenylhydrazine" instead of "*p*-nitrophenylsemicarbazone" and "*p*-nitrophenylsemicarbazine."

NEW BOOKS.

Elements of Physical Chemistry. By HARRY C. JONES, Professor of Physical Chemistry in the Johns Hopkins University. Fourth edition, revised and enlarged. New York: The Macmillan Company, 1915. Pp. xiv + 672. Price, \$4.00.

With a comparative page increase of about 20%, this fourth edition retains most of the characteristics of the first edition of the work, which appeared in 1902. "Considerable new matter has been incorporated in the fourth edition of this work. Since the book is now large enough for the purpose which it was meant to fulfill, this has been done in the smallest space possible. The new material has, for the most part, been inserted at the ends of the several chapters, to avoid, as far as possible, destroying the plates." This quotation from the author's preface points to a conservatism which embraces general viewpoint as well as choice, arrangement and treatment of subject matter. The style is pleasing, the literature references are copious and the mechanical production of the book is excellent.

ALAN W. C. MENZIES.

THE JOURNAL
OF THE
American Chemical Society

with which has been incorporated the

American Chemical Journal
(Founded by Ira Remsen)

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC
COMPANY, SCHENECTADY, N. Y.]

THE DISSOCIATION OF HYDROGEN INTO ATOMS. III. THE
MECHANISM OF THE REACTION.

BY IRVING LANGMUIR.

Received April 17, 1916.

In Part II of this paper¹ the degree of dissociation of hydrogen into atoms has been calculated from data² on the heat losses from highly heated wires in hydrogen at various pressures. In this calculation it was necessary to make certain assumptions regarding the mechanism of the processes occurring on and around the wire. The remarkable agreement between the theory thus derived and the experimental results, furnished ample justification for the assumptions, but did not necessarily indicate that the particular mechanism assumed was the only one which would lead to similar agreement.

The writer has recently developed a theory³ of heterogeneous reactions which throws a great deal of light on the mechanism of such reactions. Applied to the dissociation of hydrogen around a heated wire, this theory

¹ THIS JOURNAL, 37, 417 (1915).

² Part I, Langmuir and Mackay, THIS JOURNAL, 36, 1708 (1914).

³ This theory has, as yet, been only very briefly described (THIS JOURNAL, 38, 1139 (1915) and *J. Ind. Eng. Chem.*, 7, 348 (1915); *Phys. Rev.*, 6, 79 (1915)), but will serve as the basis of a series of papers to appear in THIS JOURNAL and in the *Physical Review*.

leads to a mechanism which may seem radically different from that previously used, but curiously enough it results in an equation identical with that obtained by the original theory.

The object of the present paper is to compare the older and the newer theories and to point out the advantages of the latter. At the same time this will serve as an illustration of the principles of the new theory and will indicate how it may be of use in the study of other heterogeneous reactions.

In the theory previously described, it was assumed that the surface of the tungsten wire contained atoms and molecules of hydrogen in chemical equilibrium with each other. The atomic and molecular hydrogen escaped from the wire at rates respectively proportional to their concentrations in the wire, while the absorption of the atoms or molecules by the wire was taken to be proportional to the corresponding pressures in the gaseous phase.

This theory led to an equation for the heat loss from the wire which proved to be in excellent agreement with experiments extending over a range of pressures from 0.01 mm. up to 760 mm. and a range of temperatures from 1000 to 3500° K. There are, however, some serious objections that may be raised against the assumption that the wire contains *concentrations* of atomic and molecular hydrogen in equilibrium with each other, and that these concentrations determine the rate at which hydrogen is dissociated by the wire. We shall see, however, that the new theory enables us to derive the same equation without making these objectionable assumptions.

The hypothesis that solid solutions of gases in metals play an important role in chemical reactions in contact with metals is a common one, and usually is not looked upon unfavorably. But it is evident that if we are to retain our ordinary conception of *concentration* the reaction must take place in a volume which contains many layers of atoms. In the experiments the range of concentrations of molecular (or atomic) hydrogen in the metal phase must have been enormous. Thus under some of the experimental conditions the concentrations were so small that the individual atoms or molecules of hydrogen were certainly separated from each other by hundreds of tungsten atoms. The rapidity of the reaction under such conditions could not possibly be very high and would be limited by the rate of diffusion of the gas through the metal.

Yet the experiments showed clearly that the velocity with which equilibrium was reached on the surface was extraordinarily high under all conditions. In fact, it was so high that practically all of the hydrogen atoms and 68% of the molecules which struck the surface reached equilibrium before leaving it again. When we consider that at atmospheric pressure and room temperature 1.1×10^{24} molecules of hydrogen strike

each square centimeter of surface per second, and that this number of molecules is contained in about 44 liters of gas, we realize the enormous velocity which this reaction must have. It is certainly impossible that such amounts of gas per second could diffuse *into* any kind of solid body and thus be brought to equilibrium.

These considerations compel us to assume that the reaction occurs directly on the surface of the metal and that it does not involve the diffusion through a film even as thin as that of a single layer of atoms.

A second difficulty arose in connection with the original theory.

At temperatures up to about 1500° K. the accommodation coefficient of hydrogen in contact with tungsten was found to be equal to 0.19. In other words, only about 19% of all the hydrogen molecules striking the filament, reached *thermal* equilibrium with it before leaving it. This figure was in good accord with the value 0.26 obtained by Knudsen with platinum at room temperature, especially when the fact was taken into account that accommodation coefficients in general appear to have slight negative temperature coefficients.

On the other hand, at high temperatures, it was found that 68% of all the hydrogen molecules striking the filament reached *chemical* equilibrium before leaving it. The original theory gave no clue to the solution of the paradox that 68% of the molecules reached chemical equilibrium, while only 19% reached thermal equilibrium. It is certainly impossible that molecules should reach chemical equilibrium while great differences in temperature still persist.

The viewpoint which has served as the basis for the new theory was gradually developed in quite other lines of work, particularly in connection with a study of the effect of gases on the electron emission from heated metals.¹ It was found that the electron emission was dependent on the composition of the actual surface layer of atoms. The deeper layers were apparently without effect. Subsequent work on gas reactions at very low pressures² indicated clearly that chemical reactions between a gas and a solid depend in general on the composition or structure of the outside layer of atoms of the solid, rather than on the thickness of an adsorbed film through which the gases diffuse.

This theory has now been developed much more completely than in any of the previously published work.

It is definitely known from the work of Bragg and others that the atoms of crystals are arranged according to space lattices in such a way that the identity of molecules is usually lost. The forces holding the crystal together are thus clearly chemical forces which act probably only between adjacent atoms. On the surface of a crystal the forces tend to be

¹ Langmuir, *Phys. Rev.*, **2**, 450 (1913); *Physik. Z.*, **15**, 516 (1914).

² THIS JOURNAL, **37**, 1139 (1915).

chemically unsaturated, and atoms or molecules of gases can thus be held firmly by the atoms of the solid.¹ In general the law of multiple combining proportions will apply. Thus each metal atom of the surface will be capable of holding a definite integral number (such as one or two) of atoms of the gas, or possibly each two atoms of metal may hold one atom of gas. The atoms held on the surface in this way will form a part of the solid body, being a real continuation of the space lattice of the solid. This layer of atoms (or molecules) on the surface may be said to be adsorbed.²

The surface of the metal is thus looked upon as a sort of checkerboard containing a definite number, N_0 , of spaces per square cm. Each elementary space is capable of holding an atom or a definite part of a molecule of adsorbed gas. The number of elementary spaces, N_0 , is probably usually equal to the number of metal atoms on the surface. But this is not essential, for we can imagine cases in which each metal atom holds, for example, two adsorbed atoms or molecules, so that we should then have twice as many elementary spaces as metal atoms on the surface.

Let us now apply this theory to the dissociation of hydrogen in contact with a heated tungsten wire. We will first calculate the rate at which atomic hydrogen condenses on the bare surface when atomic hydrogen at a pressure p surrounds the wire.

The number of grams of gas which strikes a sq. cm. of surface per second is

$$m = \sqrt{\frac{M}{2\pi RT}} p. \quad (1)$$

Let μ represent the number of gram molecules of gas striking a sq. cm. per second. Then $\mu = m/M$ or

$$\mu = \frac{p}{\sqrt{2\pi MRT}}. \quad (2)$$

Expressing p in bars,³ and placing $R = 83.15 \times 10^6$ ergs per degree, this reduces to

$$\mu = 43.75 \times 10^{-6} \frac{p}{\sqrt{MT}}. \quad (3)$$

¹ Haber (*J. Soc. Chem. Ind.*, 33, 50 (1914) and *Z. Elektrochem.*, 20, 521 (1914)) has suggested on the basis of Bragg's theory, that adsorption may be the result of unsaturated chemical forces at the surface of a solid body. Haber, however, only considers the force causing adsorption and does not take into account that the amount of adsorption depends on a kinetic equilibrium between the condensation and the evaporation of molecules.

² In a paper to appear shortly in the *Physical Review* this theory of adsorption will be developed in more detail. Preliminary accounts have already been published in THIS JOURNAL and in the *Physical Review* (*Loc. cit.*).

³ The bar is the C. G. S. unit of pressure, one dyne per sq. cm. One million bars or one megabar is equal to 750 mm. of mercury, which is more nearly average atmospheric pressure than the 760 mm. usually used.

By applying this equation, we can readily calculate the rate at which atomic hydrogen ($M = 1$) comes into contact with each square centimeter of surface. The rate at which the gas condenses to form a layer (one atom deep) on the surface will be less than the rate at which it strikes the surface for two reasons. In the first place, only a fraction α of the atoms which strike the bare surface condenses, while the fraction $1 - \alpha$ is reflected. Secondly, as the surface becomes covered with hydrogen atoms, many atoms will strike portions of the surface already covered.¹ Let θ represent the ratio of the number of vacant elementary spaces to the total number of spaces N_0 . Thus θ is the fraction of the surface which is bare. The rate at which atomic hydrogen condenses on the surface is thus equal to $\alpha\theta\mu$.

Consider the case of hydrogen molecules condensing on the surface. If each hydrogen molecule occupies only one elementary space, then the rate of condensation will still be given by the product² $\alpha\theta\mu$.

If, on the other hand, each hydrogen molecule should occupy two elementary spaces, then the rate at which molecular hydrogen would condense on the surface is equal to $\alpha\theta^2\mu$. The exponent 2 for the quantity θ is due to the fact that two adjacent spaces must be vacant simultaneously, in order that the molecule may condense. The chance that a given space, towards which a gas molecule may be moving, shall be vacant, is θ . The chance that two given spaces shall be simultaneously vacant is θ^2 .

The adsorbed atoms or molecules on the surface evaporate at a definite rate. Let the rate of evaporation in gram molecules per sq. cm. per second from a completely covered surface, be represented by ν . If θ_1 is the fraction of the surface which is covered by the atoms or molecules in question, then the actual rate at which the hydrogen evaporates is $\nu\theta_1$.

In considering the mechanism of the dissociation of hydrogen in contact with a heated wire, we may make two alternative hypotheses.

First Hypothesis.—Hydrogen exists on the surface in the form of atoms only. Molecules, formed by the combination of adjacent atoms, leave the surface immediately.

Second Hypothesis.—Hydrogen can exist on the surface in either molecular or atomic condition.

First Hypothesis.

We assume that out of all hydrogen atoms striking a bare surface, the fraction α_1 condenses and that the corresponding fraction for the molecules is α_2 .

¹ There is good reason to believe that even the hydrogen atoms which strike a surface already covered condense. But the rate of evaporation of the atoms from such a surface is so much higher than that from a bare surface that the number of atoms in the second layer is probably negligible in comparison with that in the first.

² In calculating μ in this case by (1) the value $M = 2$ will have to be used instead of $M = 1$.

Let ω be the velocity with which the dissociation of hydrogen is brought about by the heated wire. We shall express ω in gram molecules of hydrogen (H_2) dissociated per second per sq. cm. of surface.

The rate at which atomic hydrogen leaves the wire is $\nu_1\theta_1$. The rate at which it is taken up by the wire is $\alpha_1\theta\mu_1$. The net rate at which it is produced is the difference between these two, and this must be equal to 2ω . The coefficient 2 is due to the fact that two atoms of hydrogen are produced from each molecule. We thus obtain the equation

$$2\omega = \nu_1\theta_1 - \alpha_1\theta\mu_1. \quad (4)$$

In a similar way we may consider the role played by the molecular hydrogen. Since we have assumed that molecular hydrogen does not exist as such on the surface, each molecule condensing on the surface must fill two adjacent elementary spaces as two separate atoms. The rate at which molecular hydrogen is removed by condensation on the heated wire is thus $\alpha_2\theta^2\mu_2$ gram molecules per sq. cm. per second. This process will be reversible. That is, adjacent hydrogen atoms on the surface may combine together to form molecular hydrogen which then escapes from the surface. The rate at which this occurs will evidently be $\nu_2\theta_1^2$, since the chance of two hydrogen atoms occupying adjacent positions will be proportional to θ_1^2 . The coefficient ν_2 is the rate of evaporation when the surface is wholly covered by atomic hydrogen ($\theta_1 = 1$).

The difference between the two rates will be equal to ω , the rate at which molecular hydrogen disappears. Thus we obtain

$$\omega = \alpha_2\theta^2\mu_2 - \nu_2\theta_1^2. \quad (5)$$

The fractions θ and θ_1 must fulfill the condition¹

$$\theta + \theta_1 = 1. \quad (6)$$

These three equations, 4, 5 and 6, enable us to calculate the equilibrium constant in the gas phase in terms of the quantities α_1 , α_2 , ν_1 and ν_2 .

There are several possible definitions of the equilibrium constant, as follows:

$$K_p = p_1^2/p_2 \quad (7)$$

$$K_c = c_1^2/c_2 \quad (8)$$

$$K_\mu = \mu_1^2/\mu_2 \quad (9)$$

Here p_1 and p_2 are the partial pressure of atomic and molecular hydrogen in equilibrium with each other, while c_1 and c_2 are the corresponding concentrations. The third equilibrium constant K_μ as defined

¹ Provided the surface is perfectly clean. The presence of a gas (otherwise inert) which is strongly adsorbed on the surface will cause the larger portion of the surface to be covered with inert molecules (or atoms). Thus the Equation 6 becomes $\theta + \theta_1 = 1 - \theta_2$ where θ_2 represents the fraction of the surface covered by the inert substance. This theory of catalytic poisons will be developed in subsequent papers.

by (9) will be found very convenient in dealing with heterogeneous reactions. Since $p = cRT$ the relation between K_p and K_c is

$$K_p = RTK_c. \quad (10)$$

Similarly, from (2) we obtain, since $M_2 = 2$, and $M_1 = 1$

$$K_\mu = K_p / \sqrt{\pi RT} = K_c \sqrt{RT/\pi}. \quad (11)$$

In order to find the value of K_μ we place $\omega = 0$ which is evidently the condition for equilibrium. Equations 4 and 5 then reduce to

$$\mu_1 = \frac{\nu_1 \theta_1}{\alpha_1 \theta}. \quad (12)$$

$$\mu_2 = \frac{\nu_2 \theta_1^2}{\alpha_2 \theta^2}. \quad (13)$$

Whence by (9)

$$K_\mu = \left(\frac{\nu_1}{\alpha_1} \right)^2 \cdot \frac{\alpha_2}{\nu_2}. \quad (14)$$

It should be noted that θ and θ_1 cancel out in the derivation of this equation.

Since the factors α and ν are not functions of the pressure, Equation 14 expresses the law of mass action, which in this case follows automatically as a consequence of the mechanism we have assumed. From Equations 4 and 5 we can determine the values of the two factors in the second member of (14). Thus

$$\frac{\nu_1}{\alpha_1} = \frac{\frac{2\omega}{\alpha_1} + \theta\mu_1}{\theta_1} \quad (15)$$

$$\frac{\nu_2}{\alpha_2} = \frac{\theta^2\mu_2 - \frac{\omega}{\alpha_2}}{\theta_1^2}. \quad (16)$$

Substituting these in (14) gives

$$K_\mu = \frac{\left(\mu_1 + \frac{2\omega}{\alpha_1 \theta} \right)^2}{\left(\mu_2 - \frac{\omega}{\alpha_2 \theta^2} \right)}. \quad (17)$$

The value of θ may be found by solving (4) and (6) as simultaneous equations. We thus obtain

$$\theta = \frac{\nu_1 - 2\omega}{\nu_1 + \alpha_1 \mu_1} = \frac{1 - 2\omega/\nu_1}{1 + \alpha_1 \mu_1/\nu_1}. \quad (18)$$

The two Equations 17 and 18 give us a complete solution of our problem. They enable us to calculate the dissociation constant K_μ in terms of α_1 , α_2 , ν_1 and experimentally determined values of ω .

Second Hypothesis.

In this hypothesis we assume that hydrogen molecules striking the surface condense as such, each molecule occupying only one elementary

space. The atoms which strike the surface condense as atoms. Interaction between the atoms and molecules on the surface occurs.

The rate of condensation of atomic hydrogen is $\alpha_1\theta\mu_1$ while the rate at which it evaporates from the surface is $\nu_1\theta_1$. Hence we have

$$2\omega = \nu_1\theta_1 - \alpha_1\theta\mu. \quad (19)$$

This is identical with Equation 4. The rate of condensation of molecular hydrogen is $\alpha_2\theta\mu_2$ whereas the rate of evaporation is $\nu_2\theta_2$. This gives

$$\omega = \alpha_2\theta\mu_2 - \nu_2\theta_2. \quad (20)$$

The rate at which hydrogen atoms combine will be proportional to the square of θ_1 , since the chance that two atoms shall be in adjacent spaces is proportional to θ_1^2 . We may thus place the rate of formation of molecular hydrogen from the atoms, equal to $\beta_1\theta_1^2$ where β_1 is the rate of formation when the surface is wholly covered with atomic hydrogen.

The rate at which hydrogen molecules dissociate into atoms on the surface will be proportional to the product of θ by θ_2 since a hydrogen molecule must be adjacent to a vacant space in order that it can dissociate. The chance that a hydrogen molecule and a vacant space shall be adjacent to each other is evidently proportional to $\theta\theta_2$. We may, therefore, place the rate of dissociation of hydrogen equal to $\beta_2\theta\theta_2$.

We thus obtain a third equation

$$\omega = \beta_2\theta\theta_2 - \beta_1\theta_1^2. \quad (21)$$

Finally we have the condition (in the absence of catalytic poisons)

$$\theta + \theta_1 + \theta_2 = 1. \quad (22)$$

If we substitute $\omega = 0$ in Equations 19, 20 and 21, we obtain the values of μ_1 , μ_2 , etc., corresponding to equilibrium conditions.

$$\mu_1 = \frac{\nu_1\theta_1}{\alpha_1\theta}, \quad (23)$$

$$\mu_2 = \frac{\nu_2\theta_2}{\alpha_2\theta}, \quad (24)$$

$$\frac{\beta_1}{\beta_2} = \frac{\theta\theta_2}{\theta_1^2}. \quad (25)$$

Substituting (23) and (24) in (9)

$$K_p = \left(\frac{\nu_1}{\alpha_1}\right)^2 \frac{\alpha_2\beta_2}{\nu_2\beta_1}. \quad (26)$$

From (19) we obtain

$$\frac{\nu_1}{\alpha_1} = \frac{\theta\mu_1 + 2\omega/\alpha_1}{\theta_1}, \quad (27)$$

and from (20)

$$\frac{\nu_2}{\alpha_2} = \frac{\theta\mu_2 - \omega/\alpha_2}{\theta_2}, \quad (28)$$

while (21) and (25) give

$$\frac{\beta_1}{\beta_2} = \frac{\theta\theta_2}{\theta_1^2} (1 - \omega/\beta_2\theta\theta_2) \quad (29)$$

or

$$\frac{\beta_2}{\beta_1} = \frac{\theta_1^2}{\theta\theta_2} (1 + \omega/\beta_1\theta_1^2). \quad (30)$$

From (19) we obtain

$$\theta_1 = \frac{\alpha_1\theta}{\nu_1} (\mu_1 + 2\omega/\alpha_1\theta) \quad (31)$$

and from (20)

$$\theta_2 = \frac{\alpha_2\theta}{\nu_2} (\mu_2 - \omega/\alpha_2\theta). \quad (32)$$

By combining (26), (27), (28), (30) and (31), we obtain

$$K_\mu = \frac{\left(\mu_1 + \frac{2\omega}{\alpha_1\theta}\right)^2 + \left(\frac{\nu_1}{\alpha_1\theta}\right)^2 \cdot \frac{\omega}{\beta_1}}{\left(\mu_2 - \frac{\omega}{\alpha_2\theta}\right)} \quad (33)$$

Similarly, from (26), (27), (28), (29) and (32)

$$K_\mu = \frac{\left(\mu_1 + \frac{2\omega}{\alpha_1\theta}\right)^2}{\left(\mu_2 - \frac{\omega}{\alpha_2\theta}\right) - \frac{\nu_2}{\alpha_2\theta^2} \cdot \frac{\omega}{\beta_2}} \quad (34)$$

The Equations 33 and 34 are different forms of the same fundamental equation.

By substituting (31) and (32) in (22), and solving for θ we find

$$\theta = \frac{1 + \frac{\omega}{\nu_2} - \frac{2\omega}{\nu_1}}{1 + \frac{\alpha_1\mu_1}{\nu_1} + \frac{\alpha_2\mu_2}{\nu_2}} \quad (35)$$

These last three equations furnish a complete solution of our problem in the case of the second hypothesis.

Comparison with the Older Theory.

It will be interesting to compare the results obtained by each of the above hypotheses, with those found by the theory developed in Part II of this paper. The Equations 21 and 26, of Part II (page 427), correspond to the Equations 17 and 33 derived above. However, since the nomenclature previously used differs from that employed here it will be worth while to go through the derivation of the older equation again by a method which will bring out clearly the difference between the two viewpoints.

It is assumed that out of all the atoms striking the surface, the fraction

α_1 is absorbed by the metal, whereas for the molecules the corresponding fraction is α_2 . It is assumed further that the surface of the metal contains hydrogen molecules and atoms in equilibrium with each other. Let ν_1 and ν_2 be the rates at which atomic and molecular hydrogen, respectively, escape from the surface.

We may thus derive the equations

$$2\omega = \nu_1 - \alpha_1\mu_1 \quad (36)$$

$$\omega = \alpha_2\mu_2 - \nu_2, \quad (37)$$

from which we obtain

$$\nu_1 = 2\omega + \alpha_1\mu_1 \quad (38)$$

$$\nu_2 = \alpha_2\mu_2 - \omega. \quad (39)$$

It is assumed that the equilibrium inside the metal obeys the law of mass action, so that the concentration of molecular hydrogen is proportional to the square of the concentration of atomic hydrogen. It is further assumed that the rates at which each of the gases escapes from the surface, is proportional to the corresponding concentration in the metal. Thus, ν_1^2/ν_2 is a constant proportional to the equilibrium constant in the metal. Let this constant be represented by A . Then we have by (38) and (39)

$$A = \frac{(\alpha_1\mu_1 + 2\omega)^2}{(\alpha_2\mu_2 - \omega)}. \quad (40)$$

When equilibrium exists in the gas phase, we may place $\omega = 0$ and thus find

$$A = \frac{\alpha_1^2\mu_1^2}{\alpha_2\mu_2} = \frac{\alpha_1^2}{\alpha_2} K_p. \quad (41)$$

Combining (41) and (40) gives

$$K_p = \frac{\left(\mu_1 + \frac{2\omega}{\alpha_1}\right)^2}{\left(\mu_2 - \frac{\omega}{\alpha_2}\right)}. \quad (42)$$

This is the equation which was derived in Part II and which was found to be in excellent agreement with the results of the experiments. In fact, we may look upon this equation as having been proved correct by the experiments.

When we compare this equation with (17), which was calculated by the 1st hypothesis, we see that the two become identical if we place $\theta = 1$. We see by (18) that this condition will be fulfilled if ν_1 is very large, compared to $\alpha_1\mu_1$ and ω . We may thus conclude that the first hypothesis is entirely in agreement with the experiments if we assume that ν_1 , the rate of evaporation of hydrogen from the surface, is so high that only a small fraction of the surface remains covered.

If we compare Equation 42 with 33 and 34, we see that they become

identical if we take $\theta = 1$ while β_1 and β_2 are taken to be very large. This last requirement means the velocity with which adjacent hydrogen atoms or molecules interact or dissociate must be very large compared to that at which they evaporate. This is equivalent to assuming that equilibrium exists between the atoms and molecules on the surface. Thus we see that the second hypothesis is also in accord with the experiments if the rate of evaporation is assumed to be so high that only a small fraction of the surface is covered.

The experiments thus do not enable us to decide between the two hypotheses. In fact, it is also possible by means of slightly different hypotheses from those described here to obtain the same equation.

But all these hypotheses have this in common: they lead to the conclusion that only a small fraction of the surface is covered with hydrogen atoms or molecules, and that the reaction is not dependent upon phenomena occurring within the surface of the metal.

This conclusion that only a small fraction of the surface is covered with hydrogen is confirmed by other facts.

We have seen that the accommodation coefficient of hydrogen in contact with tungsten at relatively low temperatures is about 19%, whereas at high temperatures 68% of the molecules which strike the filament reach chemical equilibrium. The explanation of this apparent paradox, according to the new theory, is that the surface of the tungsten is largely covered by adsorbed hydrogen at the lower temperatures, whereas at the higher temperatures it is practically bare. The 19% thus corresponds to the fraction of molecules which condenses when they strike a surface already covered with hydrogen, while the 68% represents the fraction condensing on a bare surface.

Another fact which proves nearly conclusively that the surface of a highly heated tungsten wire is not covered to an appreciable extent by hydrogen is that the electron emission from tungsten is not perceptibly influenced by the presence of pure hydrogen.¹ A large amount of unpublished work in this laboratory has demonstrated that the electron emission affords an extraordinarily sensitive method of detecting the presence of a film of adsorbed material, so thin that it only partly covers the surface with a layer one atom deep. Some of this evidence will soon be published.

In subsequent papers, the theory of heterogeneous reactions here outlined, will be applied to a large number of reactions. It will be shown that the equations derived by Fink, in his work on the contact sulfuric acid process, may also be derived by the new theory, and that definite proof that the mechanism postulated by Bodenstein and Fink cannot apply in this work may be adduced from the experiments themselves.

¹ Langmuir, *Phys. Zeit.*, 15, 523 (1914).

The work of Bodenstein and Ohlmer on the reaction between carbon monoxide and oxygen is also in quantitative agreement with the new theory. Other cases, including several studied experimentally in this laboratory, will also be discussed.

Summary.

1. The velocity of the reaction by which hydrogen is dissociated in contact with a heated tungsten wire is so enormous that it definitely proves that the reaction cannot depend upon a diffusion of hydrogen into the metal even if the depth of penetration should be only that of a single atom.

2. A general theory of heterogeneous chemical reactions is outlined in which the reaction is assumed to take place in the actual surface layer of atoms.

3. This theory is worked through in detail for the case of the dissociation of hydrogen. It leads to equations which become identical with that previously derived by other methods, when it is assumed the hydrogen evaporates so rapidly from the surface that only a negligible fraction of the surface is covered at any time. This equation has already been shown to be in full agreement with the experiments (Parts I and II).

4. The conclusion that very little of the surface is covered is in good accord with the fact that the accommodation coefficient of hydrogen is 0.19 at temperatures below 1500° K., while the "chemical" accommodation coefficient α_2 for the dissociation of hydrogen is 0.68 at high temperatures.

5. The fact that the electron emission from heated tungsten is not affected by the presence of pure hydrogen is additional evidence that the fraction of the surface covered by hydrogen atoms or molecules must be very small.

ACCURACY OF COPPER VOLTAMETERS.

BY ASWINI KUMAR DATTA AND NILRATAN DHAR.

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When a current of moderate strength is to be measured by the copper voltameter the results given by it agree with those obtained from the silver voltameter of Rayleigh's form¹ improved upon by Richards² and his pupils. Richards considers that the improved silver voltameter can be relied upon to one part in ten thousand or more. The silver voltameter is therefore a very good register of current and we are quite justified in judging the accuracy of a copper voltameter by comparing its results with those of the standard silver voltameter. When very feeble currents are mea-

¹ *Phil. Trans.*, 175, II, 411 (1884).

² *Z. physik. Chem.*, 32, 321 (1900).

sured by the copper voltameter it is found, as a rule, that the values obtained from it are lower than those obtained from the standard silver voltameter. With a view to remove these difficulties and to find the probable causes of the inaccuracy this investigation was undertaken.¹

The arrangement of the apparatus was as usual. The street main was used as the source of current. A liquid resistance was put in the circuit, which was adjusted till the milliammeter used indicated the desired current. The surface of the copper cathode was 6 sq. cm. A slow current of carbon dioxide was bubbled through the solution in the voltameter. The current was generally passed for $2\frac{1}{2}$ – $3\frac{1}{2}$ hours, after which the copper cathode and the platinum bowl with their deposits were carefully washed, dried and weighed. It was noticed incidentally that the silver nitrate solution used in the platinum bowl lost in strength after a few days' use, probably due to partial reduction from organic matters, when the silver deposit would become loose and so the solution had to be changed from time to time in order to get a compact deposit which could easily be washed without any loss of silver deposit.

The solution generally used in the copper voltameter is that indicated by Oettel,² which is as follows: 150 g. copper sulfate, 50 g. sulfuric acid, 50 g. alcohol, 1000 g. water. First of all we tried the effect of adding sulfuric acid to the solution. 18.75 g. of recrystallized copper sulfate were dissolved in 125 cc. water (Oettel's quantity) and gradually added small quantities of acid (sp. gr. 1.745). The current was kept constant and was 10 milliamperes. The current density is therefore 0.0017 ampere per sq. cm.

TABLE I.—RESULTS OF EXPERIMENTS.

Acid added. Cc.	Silver deposit.	Copper deposit.		Error. Per cent.
		Found.	Calculated.	
0	Cu electr. blackened.
0.5	0.0873	0.0228	0.02572	11
1	0.0834	0.0226	0.02458	8
2	0.0958	0.0261	0.02823	7
3	0.0633	0.0174	0.01865	6.7
4	0.0958	0.0263	0.02823	6.9
5	0.0769	0.0208	0.02266	8.2

Thus it is found that small addition of sulfuric acid improves the result. The best effect is produced by the addition of 3–4 cc. of the strong acid in 125 cc. of the solution. Oettel's quantity 3.6 cc.

The current strength was now varied to find the range in which we can get good results by using a solution of copper sulfate and sulfuric acid only.

¹ Cf. Dhar, *Z. Elektrochem.*, 19, 746 (1913).

² *Chem. Ztg.*, 17, 543, 577 (1893).

TABLE II.

Current density.	Silver deposit, g.	Copper deposit.		Error. Per cent.
		Found, g.	Calculated, g.	
0.0033	0.1872	0.0550	0.05513	0.25
0.0025	0.1684	0.0486	0.0496	2.0
0.0013	0.0805	0.0207	0.0237	12
0.0011	0.0492	0.0126	0.0145	13
0.0007	0.0440	0.0107	0.0129	17
0.0003	0.0308	0.0068	0.0091	27

It is evident from the results of Table II that with current densities above 0.0025 ampere per sq. cm. we get accurate results even without using alcohol. As the current density falls the inaccuracy increases rapidly and reaches as much as 25% with a current density of 0.0003 ampere per sq. cm. With alcohol we get much better results but they are still unsuited for accurate work.¹ We now tried for obtaining a better substitute for alcohol and experimented with various substances. As a result of this we found that cane sugar and glucose can serve the purpose of alcohol equally well and that tartaric acid is a decidedly better substitute as the following results will show. During the course of these experiments the current was kept fairly constant and was about 7 milli-amperes, the current density being about 0.0011 ampere per sq. cm.

TABLE III.

Cane sugar added. Grams.	Silver deposit, g.	Copper deposit.		Error. Per cent.
		Found.	Calculated.	
0.0	0.0805	0.0207	0.02372	13.0
2.0	0.0731	0.0195	0.02154	9.5
4.0	0.0788	0.0219	0.02322	5.6
6.3	0.0819	0.0231	0.02413	4.3
8.5	0.0742	0.0211	0.02186	3.5
10.6	0.0908	0.0261	0.02676	2.5
14.0	0.0746	0.0217	0.02198	1.7
16.0	0.0706	0.0205	0.02080	1.4
21.0	0.0649	0.0188	0.01912	1.7
30.0	0.0858	0.0239	0.02528	5.0

The results decidedly improve with the addition of cane sugar. The best results are obtained when 15–20 g. of sugar are added per 125 cc. solution. With alcohol results of similar accuracy are obtained.²

TABLE IV.

Glucose added. Grams.	Silver deposit, g.	Copper deposit.		Error. Per cent.
		Found.	Calculated.	
2	0.0852	0.0230	0.02511	8.0
5	0.0772	0.0219	0.02275	3.7
8	0.0913	0.0262	0.02690	2.6
10	0.0746	0.0215	0.02198	2.2
14	0.0694	0.0200	0.02045	2.2
15	0.0821	0.0236	0.02419	2.4

¹ *Z. Elektrochem.*, 19, 746 (1913).

² *Ibid.*, 19, 746 (1913).

Here also we find glucose to have almost similar effect. The quantity required is about half that of cane sugar, as might be expected from its molecular weight.

TABLE V.

Tartaric acid added. Grams.	Silver deposit, g.	Copper deposit.		Error. Per cent.
		Found.	Calculated.	
0.0	0.0795	0.0201	0.02343	12.4
2.0	0.0744	0.0204	0.02192	6.8
4.8	0.0537	0.0149	0.01582	5.7
6.8	0.0750	0.0211	0.02210	4.7
9.0	0.0798	0.0226	0.02351	3.8
11.0	0.0693	0.0198	0.02042	2.9
13.0	0.0907	0.0260	0.02673	2.7
18.0	0.0858	0.0248	0.02528	1.9
23.0	0.0970	0.0283	0.02858	1.0
25.0	0.0981	0.0287	0.02891	0.73
28.0	0.0635	0.0186	0.01871	0.59
32.0	0.0967	0.0280	0.02849	0.98

Here we have a decided improvement. With the addition of only 2 g. of tartaric acid the error falls from 12% to 7% and then it gradually diminishes with the increment of tartaric acid added. With the addition of 20–35 g. of tartaric acid the error is less than one per cent.

Under these conditions we tried to vary the concentration of copper sulfate but found that Oettel's concentration gave the best results.

Now we substituted hydrogen for carbon dioxide. The experiments were carried out in a closed cell. The voltameter cell was closed with a cork fitted with two glass tubes. Through one tube a slow current of hydrogen, after being passed through two wash bottles containing potassium permanganate solution and pure water, respectively, was bubbled and the other served as an exit tube for the gas.

TABLE VI.—PASSING HYDROGEN THROUGH ELECTROLYTE.

Silver deposit, g.	Copper deposit.		Error. Per cent.
	Found.	Calculated.	
0.0924	0.0270	0.02722	0.8
0.0938	0.0275	0.02774	0.9
0.1416	0.0414	0.04173	0.7

No decided improvement is observed here by using hydrogen for carbon dioxide and using a closed cell and the error is as before about 1%.

The experiments were now conducted at about 0°. The closed cell was surrounded by ice.

ELECTROLYTE AT 0°.

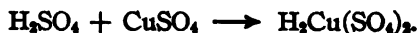
Silver deposit, g.	Copper deposit.		Error.
	Found.	Calculated.	
0.0854	0.0252	0.02517	} Practically nil
0.1382	0.0406	0.04073	
0.1013	0.0299	0.02985	

Summary.

From the above investigation we arrive at the following results:

It is immaterial whether we conduct the experiments in an atmosphere of carbon dioxide or hydrogen. Their function is only to exclude air and hence prevent the access of oxygen into the voltameter.

Sulfuric acid is essential for ensuring a good result. It prevents the hydrolysis of the copper sulfate solution, which would cause a deposition of cuprous and cupric oxide on the cathode. It also diminishes the concentration of the copper ions in the solution, due to the increase of SO_4^{2-} ions and also due to the formation of complex copper salts as indicated by the equation¹



Cane sugar and glucose can be substituted for alcohol with equal efficacy and tartaric acid is a decidedly better substitute and with it we can get good results even with feeble current strength.

It has been observed by Foerster and Seidel,² Abel and others that copper sulfate solution appreciably dissolves copper and this dissolution depends greatly on the concentration of copper ions in the solution, and also on the temperature, higher temperature favoring the dissolution. The action is more pronounced in presence of sulfuric acid which we add to prevent hydrolysis. In measuring high currents this does not materially effect the results of the experiments as the copper deposition is rather rapid, while in case of measuring feeble current the copper is deposited very slowly and the copper sulfate solution finds sufficient time to dissolve it appreciably. The dissolution of copper in this way can be very much lessened by diminishing the concentration of the copper ions in the copper sulfate solution. The improvement made by the addition of tartaric acid is probably due to its forming a very good complex with copper ions and thus diminishing the concentration of the copper ions. Functions of alcohol, sugar and glucose are probably the same as they are also known to form complexes with copper salt. This dissolution of copper is hampered by fall of temperature and so we got better results by surrounding the voltameter with ice. The low temperature also diminishes hydrolysis. But here also we have a limit. We cannot measure extremely feeble currents with fair accuracy, for in this case the deposit of copper is so very slow that the small concentration of copper ion evolved from the complex is sufficient to vitiate the result though very slightly by dissolving a little of the freshly deposited copper.

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¹ Cf. Gray, *Phil. Mag.*, 22, 400 (1886).

² *Z. anorg. Chem.*, 14, 106 (1897); Abel, *Ibid.*, 26, 1901.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF
WISCONSIN.]

THE EFFECT OF DISSOLVED SUBSTANCES ON THE VELOCITY OF CRYSTALLIZATION OF WATER. II. THE EXISTENCE OF HYDRATES IN SOLUTION AS AN EXPLANATION OF THE RETARDING EFFECT OF THE SOLUTE ON THE VELOCITY OF CRYSTALLIZATION OF WATER.

BY JAMES H. WALTON AND ALBERT BRANN.

Received March 14, 1916.

In a recent paper by the authors¹ it was shown that in the retardation of the velocity of formation of ice crystals from an undercooled solution there is a relation between the number of atoms in a molecule of the solute and its retarding effect. More recent experiments show that this relation does not always hold and in the instances cited is probably largely accidental.

The object of the present paper is to point out that *those substances that undergo hydration in solution to the greatest extent are also the substances that show the greatest retarding effect upon the V. C. (velocity of crystallization) of ice from undercooled solutions.* The experimental data that show this relationship were obtained in the manner described in the previous paper. The results are incorporated in the accompanying tables.

The investigation of the existence of compounds of solute and solvent in solution has been the subject of much investigation.² By means of conductivity, lowering of the freezing point and other measurements, Jones³ and his students have obtained data that show the relative amounts of hydration that many salts undergo in solution. Beginning with those salts that are least hydrated, the following list shows the relative hydration of some of the more common chlorides: (NaCl, NH₄Cl, KCl) LiCl·2H₂O, BaCl₂·2H₂O, SrCl₂·6H₂O, CaCl₂·6H₂O, MgCl₂·6H₂O, FeCl₃·6H₂O, AlCl₃·6H₂O. The compounds in this group that have been used by the authors are given in Table I. They retard the crystallization of water in exactly the same order, *viz.*, those most hydrated according to Jones, show here the greatest retarding effects.

In this connection the experiments of Smirnoff⁴ are of interest. This investigator determined the amount of different salts required to cause the separation of butyric acid from a 16.64% aqueous solution of the acid at

¹ THIS JOURNAL, 38, 317 (1916).

² For a review of this subject see: "Hydrates in Solution. A Review of Recent Experimental and Theoretical Contributions," E. W. Washburn, *Tech. Quart.*, 21, No. 4, Dec., 1908.

³ *Publ. Carnegie Inst.*, No. 60.

⁴ *Z. physik. Chem.*, 58, 667 (1907).

TABLE I.
The Velocity of Crystallization of 0.1 *M* Undercooled Aqueous Solutions of Chlorides.
Temp. -9.1° .

Compound.	Time per meter in seconds.	Velocity cm. per min.	Compound.	Time per meter in seconds.	Velocity cm. per min.
HCl.....	24.0	250	CuCl ₂ .2H ₂ O.....	40.0	150.0
NaCl.....	24.3	247	CeCl ₃ .7H ₂ O.....	50.0	120.0
HgCl ₂	27.7	217	MgCl ₂ .6H ₂ O.....	50.4	119.0
LiCl.2H ₂ O.....	35.5	170	ThCl ₄ .8H ₂ O.....	60.0	100.5
CdCl ₂ .2H ₂ O.....	37.1	162	FeCl ₃ .6H ₂ O.....	84.8	70.8
CaCl ₂ .6H ₂ O.....	38.6	155	AlCl ₃ .6H ₂ O.....	153.2	39.2

different temperatures. It is assumed that, owing to the fixing of part of the water by the salt, the free solvent is no longer able to retain the acid in complete solution. It is believed that this lowering of the solubility is due to hydration of the dissolved salt. The relative amounts of some of the chlorides that were necessary to precipitate the butyric acid are:¹ 0.213 NaCl, 0.191 LiCl, 0.079 CaCl₂, 0.076 MgCl₂, 0.048 AlCl₃. There is a decided parallelism between the action of these salts in precipitating the butyric acid, and their action in retarding the V. C. of water.

TABLE II.
The Velocity of Crystallization of 0.5 *M* Undercooled Aqueous Solutions of Nitrates.
Temp. -9.1° .

Compound.	Time per meter in seconds.	Velocity cm. per min.
KNO ₃	43.9	137.0
AgNO ₃	47.6	129.0
Pb(NO ₃) ₂	102.0	58.9
Cu(NO ₃) ₂ .6H ₂ O.....	500.0	12.0
Al(NO ₃) ₃ .8H ₂ O.....	1054.0	5.8

Of the compounds in Table II in which the effects of several nitrates are shown, the nitrates of aluminium and potassium have been investigated by Jones. These two salts occupy the same relative positions in his experiments as they do in ours. The experiments in Table II were carried out with 0.5 *M* solutions instead of 0.1 *M* because it was found that when the less concentrated solutions were used the differences in the effects of two salts are at times not great enough; they might be accounted for by experimental error.

The sulfates (Table III) show an abnormal behavior. Sodium sulfate, for example, in spite of its large content of crystal water has a comparatively slight retarding effect. Aluminium sulfate retards the V. C. more than any other substance used in these experiments. The behavior of the sulfates of zinc and magnesium is very interesting. A tube of the freshly prepared solution of each of these substances was undercooled and allowed to crystallize. The contents of the tube were warmed until

¹ See Senter, *Trans. Faraday Soc.*, 3, 149 (1907).

TABLE III.

The Velocity of Crystallization of 0.5 *M* Undercooled Aqueous Solutions of Sulfates.
Temp. -9.1° .

Compound.	Time per meter in seconds.	Velocity cm. per min.	Compound.	Time per meter in seconds.	Velocity cm. per min.
K_2SO_4	71	84.5	$ZnSO_4 \cdot 7H_2O^1$	202	..
$(NH_4)_2SO_4$	83.7	73.4		170	..
$Na_2SO_4 \cdot 10H_2O$	137	44.0		170	..
$CuSO_4 \cdot 5H_2O$	177	33.9		150	..
$MgSO_4 \cdot 7H_2O^1$	218	..	$FeSO_4 \cdot 7H_2O$	200	30
	194	..	$Al_2(SO_4)_3 \cdot 18H_2O$..	3000	2
	184	..			
	177	..			
	174	..			

everything was dissolved and the cooling and crystallizing were repeated. With the successive experiments, using the same solution, the retarding effect of the solute became less. Jones found that the sulfates in general gave abnormal results in his experiments. This he believes to be due to association of molecules of the solute. The behavior of the two salts just mentioned can be explained by this hypothesis, providing that the association of the molecules takes place with measurable velocity. The association would mean a lowering of the molecular concentration and a diminishing of the retarding effect of the solute.

Sodium bromide crystallizes with two molecules of water of crystallization while potassium bromide is anhydrous. These two salts should show different degrees of hydration in solution, and measurements of freezing point lowerings show this to be the case. To find out whether or not equivalent solutions of these salts have the same retarding effect on the V. C. of water, measurements were made with solutions of potassium bromide and sodium bromide in which the concentrations varied from one-eighth to one gram molecule per liter. The results are given in Table IV and are

TABLE IV.

The Velocity of Crystallization of Undercooled Aqueous Solutions of Potassium and

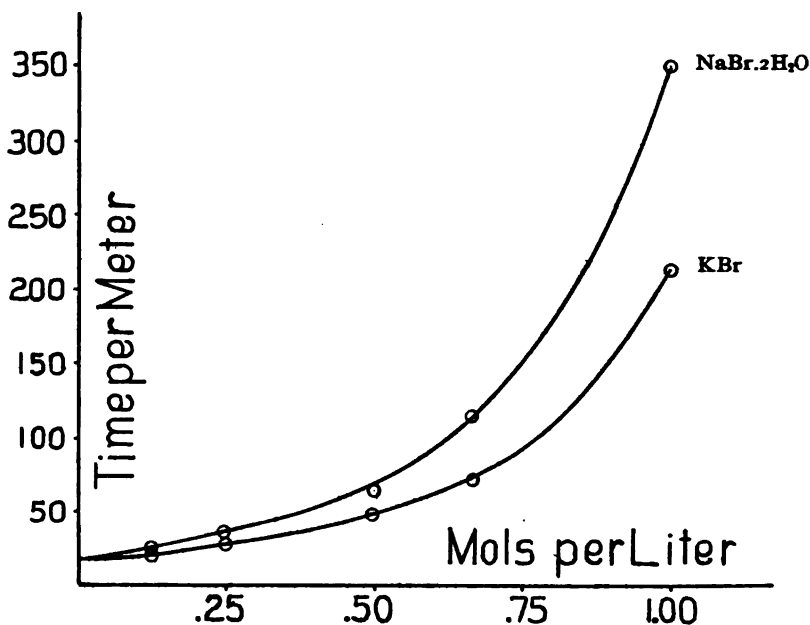
Sodium Bromides.		Temp. -9.1° .	
KBr Mols per liter.	Time per meter in seconds.	NaBr Mols per liter.	Time per meter in seconds.
1.00	212.0	1.00	350.0
0.67	78.2	0.67	114.0
0.50	49.5	0.50	63.8
0.25	29.6	0.25	37.0
0.125	23.1	0.125	27.0

shown graphically in the figure. At all concentrations measured the retarding effect of the sodium bromide was much greater than that of an equivalent solution of the potassium bromide. This is again in agreement with the work of Jones, who found that the sodium bromide is more hydrated in solution than the potassium bromide.

¹ V. C. not constant. Values represent repeated trials with the same solutions.

In the light of the following statement¹ the influence of glucose upon the V. C. is interesting:

"In connection with the results obtained by Roth (*Z. physik. Chem.*, 43, 560 (1903)) for glucose one point is worthy of mention. Roth found that freshly prepared solutions of glucose gave smaller values for the molecular lowering than did the same solutions after standing for a few days. The increase in the molecular lowering with the time corresponded to the decrease in the birotation. Hydration has been suggested as a possible explanation of this result, and this is probably true."



Two 0.5 *M* solutions of glucose (a) and (b) were prepared, the former from anhydrous and the latter from the crystallized substance, which has one molecule of water of crystallization. The V. C. of the two freshly prepared solutions was measured, they were then allowed to stand for ten days and measurements were again made. The time necessary for the crystals to fill a tube one meter in length was as follows:

Glucose (a) Feb. 10, 271 sec.

Feb. 19, 303 sec.

Glucose (b) Feb. 10, 320 sec.

Feb. 19, 320 sec.

This experiment indicates that the more the glucose is hydrated the more it retards the V. C. of water.

By measuring the V. C. of 0.5 *M* solutions of various potassium salts, it has been possible to learn the effects of the different negative radicals. The results are given in Table V. Relative hydration values for these salts have been determined by Jones, Smirnoff, Biltz.² Their results do

¹ Washburn, p. 374.

² *Z. physik. Chem.*, 40, 185 (1902).

not entirely agree as to order with the data in Table V but there is a general agreement, however.

TABLE V.

The Velocity of Crystallization of 0.5 *M* Undercooled Aqueous Solutions of Potassium Salts. Temp. -9.1° .

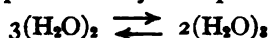
Compound.	Time per meter in seconds.	Velocity cm. per min.	Compound.	Time per meter in seconds.	Velocity cm. per min.
KNO ₃	43.9	137	KCl.....	57.8	104.0
KSCN.....	46.8	128	K ₂ SO ₄	71.0	84.5
KBr.....	49.5	121	KCN.....	99.3	60.4
KI.....	51.1	117	KF·2H ₂ O....	184.0	32.6

In addition to the foregoing experiments there are a number of others that are also explained by the hydration theory. Urea and glyocoll are not hydrated to any extent; the retarding effects of these substances on the V. C. of water is inconsiderable. Cane sugar is hydrated to a great extent; its retarding effect is marked.

In the first paper the effect of certain of the alkaloids was shown to be great, even when they are present in as low a concentration as 0.02 *M*. The substances used were: cocaine hydrochloride, quinine bisulfate and brucine sulfate. The last three of these compounds have two, seven, seven molecules of water of crystallization, respectively, indicating the formation of hydrates in the solution.

Conclusion.

The experimental data in this paper and in the first communication on this subject are best explained by the hydrate theory. The formation of ice crystals may be represented by an equation similar to the following:



The existence of a part of the solvent in combination with the solute would mean that this combination would have to be broken before crystals could form, consequently the formation of ice crystals in a solution containing a solute that is hydrated would be much slower than their formation from the pure solvent.

The authors do not for one moment believe, however, that the retardation is entirely due to the presence of hydrates in the solution. The heat evolved when ice crystals separate is different for different solutions; the lowering of the freezing point varies to a certain extent with the solute, consequently at the same temperature equimolecular solutions of different compounds may not be equally undercooled; the viscosity, the heat of ionization and the thermal conductivity of the solutions are also factors that must be taken into consideration. In concentrated solutions these factors are doubtless of considerable importance; in dilute solutions the authors believe that the retardation is almost entirely due to the existence of hydrates.

It is of interest to note that in solutions as dilute as 0.1 *M* there is a marked difference between the behavior of those substances that are hydrated, and those that form hydrates to an inconsiderable extent only. This investigation is being continued.

MADISON, WISCONSIN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MANITOBA.]

SUPERSATURATED SOLUTIONS OF LIQUIDS IN LIQUIDS.

BY HAROLD S. DAVIS.

Received February 10, 1916.

It is comparatively easy to form supersaturated solutions of solids or gases in liquids, but, up to the present, attempts to form similar supersaturated solutions of liquids in liquids have met with little success.

Rothmund¹ has considered the possibility of the existence of such supersaturated solutions. His criterion for such a condition is based on the following considerations: A small drop of liquid is more soluble than a larger one and a solution can be supersaturated until it is in equilibrium with the smallest drops which are already formed in the liquid. When this concentration is exceeded, these drops rapidly grow, becoming less soluble as they do so and soon reduce the concentration of the supersaturated solution to that of a saturated one. In a case where the solubility increases with the temperature, the cooling of the solution causes drops to appear somewhat below the temperature of saturation for that particular concentration; but when the solution is heated, the larger drops will persist until slightly above the temperature of saturation. That is, there will be a difference between the temperatures at which the cloudiness appears and disappears and the greater the degree of supersaturation, the greater will be the difference in temperature.

In the case of all the liquids he investigated, this difference of temperature was very small; hence Rothmund concluded that there was no evidence of supersaturation.

Füchtbauer² carried out some experiments which seemed to give strong evidence of the existence of supersaturated solutions of liquids in liquids. He came to the conclusion that the difficulty in forming supersaturated solutions of liquids in liquids is due to the presence of dust particles or foreign nuclei of some sort, perhaps colloids.

A careful examination of the effect of dust particles on preventing the formation of supersaturated solutions of liquids in liquids was made by Fawcett.³

¹ *Z. physik. Chem.*, 26, 443 (1898).

² *Ibid.*, 48, 566 (1904).

³ Thesis, University of Toronto, 1912. For summary see E. Fawcett, *Proc. Roy. Soc. Canada*, 1913. (I am indebted to Prof. F. B. Kenrick for a copy of this thesis.)

The method he used to detect supersaturation was similar to that used by Rothmund as already described above, that is, the determination of the difference between the temperatures at which the cloud appears and disappears when the temperature of the solution is changed. In every case there was a difference between the two temperatures, but it was of the order of the experimental error. He then attempted to remove the dust particles by various methods but again no evidence of supersaturation was obtained.

Liesegang¹ has pointed out that even if dust particles, or foreign nuclei of any kind, do facilitate precipitation of the second liquid phase, before the metastable limits of supersaturation are exceeded, yet that does not necessarily make it impossible to exceed these limits in a solution which contains such nuclei. For the nucleus prevents supersaturation only by forming a zone of approximately normal concentration at its surface, toward which the solute diffuses and as the rate of diffusion is not, after all, very fast, the influence of the nuclei in preventing supersaturation is dependent on the time in which the supersaturated state is obtained.

Experimental Determination of the Degree of Supersaturation of Some Liquids in Liquids.

Phenol in Water.—The *phenol* used in these experiments was a pure grade of material, which was fractionally distilled before use.

The water used in all this work was prepared as follows: Ordinary distilled water was subjected to fractional distillation in a still of the type designed by Bousfield, obtained from Messrs. Baird and Tatlock. Although this method is guaranteed to give water of a high degree of purity, it was not free from suspended particles visible to the naked eye. It was kept in well-stoppered hard glass bottles. High purity of the water could only be maintained where all later experimentation was done in sealed glass vessels. In other cases where cork stoppers were used, ordinary distilled water undoubtedly would have done just as well.

A thermostat with two parallel glass sides was regulated at 25°. It maintained a temperature constant to a few hundredths of a degree.

The solubility of phenol in water increases continuously with the temperature from 0° to the critical solution temperature.² Solutions of phenol and water saturated at 25° were formed in two ways:

1. By stirring with a current of air for half an hour. This air was first heated to the temperature of the thermostat by drawing it through a copper coil immersed in a bath at 25°.

2. By heating to a higher temperature and then cooling to the temperature of the bath. A dense cloud formed, showing that the solution was now saturated at 25°.

¹ *Kolloid. Z.*, 3, 76 (1915).

² Alexjew, *Wied. Ann.*, 28, 305 (1886); also Rothmund, *Loc. cit.*

Various forms of tubes were used to hold the solutions. A very convenient form was found to be test tubes 20 cm. long and 2.5 cm. in diameter. Two Beckmann thermometers, graduated into hundredths of a degree, were regulated so that they read the same, at the same temperature, to less than a hundredth of a degree. One was placed in the thermostat, the other, through a tight fitting rubber stopper, in the test tube to be examined. The test tube was then cooled by bringing it into the room or by immersion in a beaker of water at a temperature below 25°.

The conclusion drawn from a large number of experiments of this kind was, that a clear saturated solution of phenol in water at 25° shows a distinct cloud on precipitation of the second phase before it has cooled a tenth of a degree.

Aniline and Water.—The solubility of aniline in water at ordinary temperatures increases with the temperature.¹ Solutions of aniline in water showed no marked evidence of supersaturation, although the measurements were not done with as much care as in the case of phenol solutions.

Nitrobenzene and Water.—The nitrobenzene used was a material from a well-known firm. It was shaken for several hours with calcium chloride and then distilled. As will be shown from experimental data, the solubility of nitrobenzene in water increases from temperatures well below 20° to one above 50° and that of water in nitrobenzene also increases over these limits. The method of procedure in the measurement of the supersaturation was therefore similar to that already described in the case of phenol and water.

(A) at 25°.—Five test tubes containing nitrobenzene and water were placed in the thermostat and the solutions in them well stirred with air for three hours. They were then tightly stoppered and allowed to stand till the solutions were clear. A Beckmann thermometer was placed in one of the tubes, which was then taken out of the thermostat and allowed to cool to room temperature. The bulb of the thermometer was so large that it probably did not accurately record the temperature of that particular part of the solution in which a cloud first appeared. Invariably a cloud quickly appeared in the lower layer of nitrobenzene with a little dissolved water, before any appreciable lowering of temperature was noticed; but the upper layer remained clear until a perceptible degree of supersaturation had been obtained. The results were as follows in three tubes examined:

No. of tube.....	1	2	3
No. of degrees of supersaturation.....	0.6°	0.1°	0.3°

(B) at 20°.—It was thought that the solution at 25° might not have been saturated, either because the stirring was not sufficient or because

¹ Alexjew, *Loc. cit.*

the cork stopper had permitted vapor to escape. So two similar tubes were sealed up in the blowpipe. They were heated to 40° , shaken and allowed to settle, then placed in a thermostat¹ at 20° , constant to less than 0.1° . A dense cloud appeared, proving that the solutions were saturated, since the solubility of nitrobenzene in water appears to increase continuously from 0° to 50° . The solutions were allowed to stand in the thermostat until they were clear and investigated for supersaturation as described above.

Supersaturation in lower layer.....	Tube (1) 0.07°	Tube (2) 0.00°
Supersaturation in upper layer.....	1.3°	0.3°

The Solubility of Nitrobenzene in Water.—No data exist on the solubility of nitrobenzene in water. Accurate measurement of the solubility of such a sparingly soluble substance is exceedingly difficult. The thermometers used in the solubility measurements were made of normal glass and graduated to 0.1° . They had been standardized in the Physikalisch-technische Reichsanstalt.

The solubility at 20° was determined by a method similar to that used by Rex.² The neck of a 1000 cc. flask was drawn out and to it was sealed an oblique T tube. One end of this was sealed and formed a graduated measuring tube which was carefully calibrated with weighed amounts of mercury. The terminal part of this measuring tube was 0.5 cm. wide and 5 cm. long. It then broadened out to a width of 1 cm. Thus the same apparatus could be used to measure changes of volume of two different orders of magnitude.

The apparatus was weighed and the main body of the flask nearly filled with distilled water. Some nitrobenzene saturated with water at 20° was poured down a capillary funnel into the measuring tube. The apparatus was then evacuated, sealed up in the blowpipe and weighed. After bringing the apparatus to the temperature of 20° , the volume of the nitrobenzene was read off. The nitrobenzene was now allowed to run into the main part of the flask. This was heated to 30° , well shaken up, and after some time put in the thermostat at 20° . A dense cloud formed, showing that the solution was saturated. The flask was shaken in the thermostat for many hours and the volume of the residual nitrobenzene determined in the measuring tube. The great source of error was in the presence of small drops that would not coalesce.

The result of one determination was that 100 g. of solution dissolve 0.16 cc. of the nitrobenzene saturated with water. The specific gravity

¹ This thermostat was controlled by an alternating current thermoregulator which has been described in *THIS JOURNAL*, 37, 1520 (1915). A better form was described by McDermott in *THIS JOURNAL*, 37, 2381 (1915). I have adopted his form and find it gives great satisfaction.

² *Z. physik. Chem.*, 55, 358 (1906).

of nitrobenzene saturated with water at 20° was found to be 1.20 \times . Subsequent work shows that the amount of water in this nitrobenzene may be neglected. Hence, the solubility of nitrobenzene in water thus obtained was 0.19 g. per 100 g. of solution.

So far, the method is very similar to that employed by Rex. He determined solubilities at 30° in the same way, but the following method will be found useful in certain cases: Qualitative experimentation soon shows that the solubility of nitrobenzene in water increases continuously from 20° to 30°. Water, therefore, was saturated with nitrobenzene at 30° and the clear solution forced over into the flask above described. This was sealed off, cooled to 20° and the volume of the precipitated nitrobenzene determined. A preliminary experiment gave 0.021 cc.; a more careful one, 0.025 cc. or 0.03 g., as the increase in the solubility of nitrobenzene in water from 20° to 30°. While this value must be considered fairly satisfactory, the absolute value for the solubility at 30° depends on the value at 20°.

As a check on these values, the solubility of nitrobenzene in water at about 55° was determined by the cloud method so well described by Rothmund.¹ Known weights of pure nitrobenzene and water were sealed up in a tube and the temperature found, at which the cloud of precipitation of the second phase appeared and disappeared.

Wt. of nitrobenzene, 0.290 g.; wt. of water, 107 g.; cloud appeared, 54.2°; cloud disappeared, 55.5°; mean, 55°. These temperatures were not sharply marked.

The collected results are:

Temperature.....	20	30	55
Solubility of nitrobenzene in water. (Grams per 100 g. soln.)	0.19	0.22	0.27

These results should only be regarded as showing the order of the values for the solubility, but the method is capable of yielding good results.

The Solubility of Water in Nitrobenzene.—This was determined by the cloud method outlined above. For the lower temperatures the heating bath was water; for the higher, melted paraffin.

Cenc. soln. (g. H ₂ O : 100 g. soln.)	Temp. of appearance of cloud.	Temp. of disappearance of cloud.	Mean of the two.
0.174	8.4°	9.3°	8.8°
0.194	14.2°	15.2°	14.7°
0.299	29.8°	31.8°	30.8°
0.401	43.2°	45.3°	44.2°
0.713	62.3°	64.4°	63.3°
1.53	105.0°	108.2°	106.6°

Carbon Disulfide and Water.—The carbon disulfide used in these experiments was a pure grade which was shaken up for many hours with successive portions of sulfuric acid until the acid showed no color on such

¹ Rothmund, "Löslichkeit und Löslichkeitsbeeinflussung," 1907, p. 30.

treatment. It was then washed free from acid with distilled water, shaken for six hours with calcium chloride and distilled.

In contradistinction to the other liquids dealt with in this paper, the solubility of carbon disulfide in water decreases continuously from 0° to 50° . Chancel and Parmentier¹ determined the solubilities by chemical estimation of the amounts of disulfide in the saturated solutions. Rex² measured the volumes dissolved on solution as already described in this paper. A glance at Curve I shows that the results obtained by the



Fig. 1.—Solubility of Carbon Disulfide in Water.

Curve I, Rex's values (grams carbon disulfide in 100 g. solution).

Curve II, Chancel and Parmentier's values (grams carbon disulfide in 100 liters solution).

two methods do not agree, either for the form of the solubility curve or for the absolute values of the solubility. I found that the solubility increases again above 50° , because solutions saturated at 60° or 70° showed a dense cloud on cooling. More work on the solubilities of these sparingly soluble substances is greatly to be desired.

Test tubes 20 cm. long and 2.5 cm. in diameter were nearly filled with a mixture of carbon disulfide and water and closed with a good tight fitting cork. The solutions were cooled to about 10° , shaken (prolonged shaking is not required) and allowed to settle. When now the tubes were put in a thermostat at 20° constant to 0.1° , a dense cloud appeared in the water layer, which must, therefore, have been saturated with carbon disulfide at that temperature. The cloud slowly settled and disappeared. Often, however, a slight milkiness remained. So, just before heating

¹ *Compt. rend.*, 99, 892 (1894); 100, 773 (1885).

² *Z. physik. Chem.*, 55, 358 (1906).

the solutions above 20° , they were cooled to $10-15^{\circ}$ for a short time, when the water solution became very clear.

The solutions were heated above 20° in the following way: A tall, narrow beaker was partly filled with water at a temperature of about 18° and water at a temperature of about 70° was poured upon this down a wire, at the base of which was a small watch glass. This watch glass was held in a horizontal position by the wire and broke the fall of the water, so that two layers of water at very different temperatures were obtained. Into the beaker was plunged one of the test tubes described above. A cloud at once appeared in the top of the upper layer, i. e., the solution of carbon disulfide in water, and slowly moved down the tube. The temperature of the water just ahead of this cloud was investigated by a small boiling point thermometer with a bulb only 8 mm. in length, so that the temperature in a local spot in the liquid could be determined. It was found that clear spaces beneath the cloud had temperatures as high as $23-24^{\circ}$ while it must be remembered that this solution was saturated at 20° .

Two of the experiments were performed with sealed tubes, which were broken open at the top to admit the thermometer just before heating above 20° . In this way any errors arising from the use of corks were eliminated, but these solutions behaved the same as those kept in corked tubes.

Effect of Mechanical Jar on Supersaturated Solutions of Liquids in Liquids.

It is well known that supersaturated solutions of solids and gases in liquids are particularly sensitive to a mechanical jar. A single experiment shows this very well in the case of a gas dissolved in a liquid.

If a solution of air in water, saturated at atmospheric pressure, is placed in a stout tube such as a Nessler tube, and if the pressure is lowered by connecting it to an aspiration pump, then a supersaturated solution is obtained. A few bubbles form and rise to the surface, after which the solution remains quiet. If now the tube is struck sharply on the side with a glass rod, hundreds of bubbles appear inside the liquid.

It was noticed in the case of solutions of phenol and nitrobenzene in water, that sometimes, on striking the thermometer a blow, clouds seemed to come off it. The existence of such a phenomenon was clearly established in the case of solutions of carbon disulfide in water, in the following way: A 500 cc. flask was filled with a clear solution of carbon disulfide, saturated at 20° . A stout glass rod (7 mm.) was flattened on the bottom to a disk about $1\frac{1}{2}$ cm. wide. It was supported in the solution through a cork. When the flask was placed in a beaker of water at 35° , a cloud formed at the top of the solution and moved slowly down. Now, while the disk of the rod was still in a clear part of the solution, the top was struck a sharp blow with a small iron clamp, upon which clouds were

observed to come from the bottom of the rod and to form also in the solution below it: Sometimes the cloud formed after a few seconds, nearly a centimeter below the disk.

Calculations of the Degrees of Supersaturation Theoretically Possible for Solutions of Liquids in Liquids.

Kenrick¹ has suggested that there is no essential difference between supersaturated solutions of solids in liquids and those of liquids in liquids, but that "the cause of the small degree of supersaturation of liquids is connected with the comparatively small surface tension of the interface between liquid and liquid." Ostwald² was the first to derive a formula showing the change in the solubility of a particle of solid or liquid with size. This formula has been corrected by Freundlich,³ who gives one of the following form:

$$\ln \frac{S_1}{S} = \frac{2M\sigma}{R\theta\rho r}$$

S is the solubility of a substance for particles of infinite radius.

S_1 is the solubility for particles of radius r .

M is the molecular weight of the substance in solution.

σ is the interfacial surface tension.

R is the gas constant (8.3×10^7 ergs/degree).

θ is the absolute temperature of the solution.

ρ is the density of the particles.

(All quantities are expressed in absolute units.)

From this formula, the supersaturation, theoretically possible, has been calculated for the following substances, assuming that in each case a particle of radius 15×10^{-7} cm. can be formed spontaneously in the supersaturated solution:

$$R = 8.3 \times 10^8 \frac{\text{ergs}}{\text{degree}}; \theta = 298^\circ; r = 15 \times 10^{-7} \text{ cm.}$$

Solution.	σ .	M .	ρ .	Percentage supersaturation calc.	Super-cooling calc.	Super-cooling found.
Calcium sulfate in water..	550 ⁴	136	2.32	600
Isobutyric acid in water..	1.76 ⁴	88	0.95	0.8
Nitrobenzene in water....	23 ⁵	123	1.20	12	8°	0.1° to 1.4° ⁶
Water in nitrobenzene....	23	18	1	2	0.8°	0.0° to 0.7° ⁶
Carbon disulfide in water.	38.4 ⁵	44	1.23	7	$\left[\begin{smallmatrix} 6^\circ \\ 25^\circ \end{smallmatrix} \right]$ ⁷	3°
Water in carbon disulfide.	38.4	18	1	4

¹ *University of Toronto Studies*, 99, 4 (1913).

² *Z. physik. Chem.*, 34, 504 (1900).

³ H. Freundlich, "Kapillarchemie," 1909, p. 144.

⁴ F. Kenrick, *Loc. cit.*

⁵ Mlle. L. van der Noot, *Bl. Acad. Belg.*, 4, 501.

⁶ The results obtained at 20° are also included.

⁷ The 6° is obtained from the values for the solubility of carbon disulfide in water

In these calculations it has been assumed that a drop with a radius of the order 1.5×10^{-8} can be formed spontaneously in the solution. It will be well now to review allied phenomena to see if there is any ground for such a belief.

The Spontaneous Formation of Nuclei in Gases.

The conditions of condensation of water vapor in air and other gases have been carefully investigated by C. T. R. Wilson¹ and Barus.² Their experiments showed that nuclei are always present in large numbers, sufficient to condense the vapor when it has about eight times its normal density. He showed that drops with a radius of the order 10^{-8} cm. would, according to accepted formulae, be in equilibrium at this eight-fold density and that such drops would contain but a few molecules. He suggested that such drops might be formed spontaneously through the accidental collision of molecules.

J. J. Thomson³ has offered the following theory to explain the phenomena attending the condensation of water vapor from gases:

"When a liquid film gets very thin, its surface tension no longer remains constant but depends on its thickness. For very thin films, theory indicates⁴ that the surface tension would be proportional to the square of the thickness, while the experiments of Reinold and Rücker⁵ showed that the surface tension had a maximum value for a thickness comparable with that of the dark spot in soap films. More recent experiments by Johannot⁶ have made it probable that, considering the surface tension as a function of thickness, there is more than one maximum.

"We see now when we take the variation of surface tension into account that even the slightest supersaturation will produce some condensation, but that these drops will be exceedingly small and will evaporate as soon as the supersaturation ceases."

He then shows that if supersaturation increases, drops may finally be formed of such radius that they will continue to grow as long as supersaturation exists and will produce a dense cloud. On the contrary, on the evaporation of a drop, *it may persist at a temperature somewhat above* obtained by Chancel and Parmentier (*Compt. rend.*, 99, 892 (1884); 100, 773 (1885)), the 25° from the values obtained by Rex (*Z. physik. Chem.*, 55, 355 (1906)). The value 0.201 found by Rex at 20° is incorrectly copied as 0.101 in the *Chem. Zentralbl.*, 1906, p. 1594.

¹ *Phil. Trans.*, (A) 265 (1897) and (A) 403 (1899).

² *Publ. Carnegie Institution of Washington* No. 40, 149 (1906); also No. 62, No. 96, I and II and *Smithsonian Contributions*, 34 (1905).

³ Thomson, "Conduction of Electricity through Gases," 183 (1906).

⁴ See Lord Rayleigh, *Phil. Mag.*, 5, 33.

⁵ Rücker and Reinold, *Phil. Trans.*, 177, II, 627 (1886). Bakker (*Phil. Mag.*, [6] 17, 341 (1909)) disputes this conclusion. From prolonged mathematical consideration he concludes that "it follows that the capillary layer must always be complete and the apparition of the black spots cannot be explained otherwise than as the consequence of a temporary and local diminution of the surface tension in the considered points in consequence of the temporary and local increase of evaporation in these points."

⁶ *Phil. Mag.*, 47, 501 (1899).

the saturation temperature for that concentration of water vapor, but that a temperature will finally be reached where it will disappear.

Opalescence near the Critical Temperature.

As is well known, gases in the critical condition show a marked opalescence: "It appears only inside a few tenths of a degree and certain volume limits from that point. Also under suitable conditions just before the disappearance of the meniscus, it appears in the liquid just as well as in the gas after the disappearance of the liquid into the common phase."¹

A similar phenomenon appears in solutions of liquids in liquids near the critical solution temperature, which is thus described by Rothmund:²

"This cloudiness appears blue in incident, and brown-red in transmitted light. It is strongest in the immediate neighborhood of the critical temperature and decreases slowly as the temperature changes till it completely vanishes. Still, this takes place gradually and a definite point cannot be established at which it can no longer be seen. It can often be clearly recognized at temperatures which are ten degrees or more removed from the critical temperature. - - - As a rule, it does not appear at the separation of a new liquid phase from a solution but only in the neighborhood of the critical point.

"From the whole behavior of this phenomenon it is evident that it is to be sharply differentiated from the precipitation of drops of the second phase which precedes the separation into two layers. The latter is accompanied by a thick clouding which immediately makes the liquid opaque and in a longer or shorter time leads to the formation of a sharp surface of separation. On the other hand it is always possible to see through a critically clouded solution. - - - From the theoretical standpoint, too very strong objections can be raised against that idea. For if one has to deal here with precipitated drops of the same kind and with the same properties as the drops which are visible under the microscope, these could not remain stable as small drops but must grow."

Konow³ has attempted to explain this peculiar opalescence as due to the influence of foreign dust particles.

F. G. Donnan⁴ has given a complete theory of the opalescence observed at the critical point of a liquid and Rothmund has applied it further to explain the opalescence at the critical solution temperature.

Donnan makes the following assumptions:

(a) Below the critical temperature, the interfacial tension between the two phases is positive for all values of the radius of curvature.

(b) At the critical temperature the interfacial tension becomes zero for all ordinary curvatures, but remains positive for very small values of the radius of curvature. *It will be seen that this assumption involves*

¹ Smoluchowski, *Ann. phys.*, [4] 25, 217 (1908). This article contains a good list of references.

² Rothmund, "Löslichkeit u. Löslichkeitsbeeinflussung," 1907, p. 76. This is the best exposition of the subject and contains complete references.

³ Drude's *Ann.*, 10, 360 (1903).

⁴ *Chem. News*, 90, 139 (1904).

the further one, that at the temperature of disappearance of the meniscus at a boundary surface of ordinary curvature, the two phases do not become identical.

(c) At temperatures slightly above the critical, the interfacial tension is still positive for very small radii of curvature, but negative for all ordinary curvatures, while at a still higher temperature it becomes negative for all curvatures.

Granted these assumptions, the existence of permanent opalescence above the ordinary critical temperature follows at once. It will be seen that there is a great deal in common between the theories of Donnan and Thomson.

Smoluchowski¹ has brought forward the idea that the opalescence observed at the critical temperature and that observed at the critical solution temperature are due to the inequalities of density, which, according to the kinetic theory, must exist in matter, due to the movements of the molecules. He has brought forward evidence that these fluctuations become noticeable when a liquid is in the critical state, on account of the greatness of the compressibility at that point, through which regions with considerable difference in density may be nearly in equilibrium with each other.

The critical opalescence according to him is not caused by true drops but by "diffuse heaps of indeterminate size, since for every volume there corresponds a different density." Further, "it is not unreasonable to suppose that the life of such agglomerations is greater in the critical condition."

Smoluchowski gives the following criticisms of Donnan's hypothesis:

"This hypothesis seems to me unsatisfactory in several respects: In the first place we are dealing here not with two different substances, but with one substance whose two phases have already become identical at the critical point. What is this liquid then? Its existence above the critical temperature must first be proved. And why does the opalescence also appear below that temperature? Moreover, the ordinarily accepted views on capillary force seem to correspond to a decrease in the surface tension with decrease in the radius of curvature, rather than with the reverse. Finally, we will not go into a prolonged discussion of these questions, since Donnan's hypothesis in view of the simple molecular kinetic explanation of those phenomena seems to be completely unnecessary."

Apparently he has misunderstood Rothmund's application of Donnan's hypothesis, for regarding the unchangeability of the phenomena with time he says:

"This condition renders more difficult Rothmund's explanation of the phenomenon through suspended drops, since, according to Lord Kelvin's rule, the large drops must grow at the expense of the smaller; that is, the phenomenon must change in the course of time."

That Smoluchowski's views afford a profound view into the nature of

¹ *Loc. cit.*

matter cannot be doubted, but it is not yet clear that they afford a complete explanation of the critical opalescence. In the first place, no evident reason has been given as to why the life of an agglomeration should be greater at the critical point. Moreover, if the fluctuations in density in the case of a gas become more noticeable at the critical point because of the great compressibility at that point, how can similar reasoning be applied to explain the opalescence at the critical solution temperature?

Furthermore, his objections to Donnan's theory are not convincing. It has already been pointed out that his contention that small drops must be unstable because of the increase of vapor pressure is not true, if Donnan's assumptions are granted. One of these assumptions, the increase in the value of the surface tension and the stability of drops above the saturation temperature, has been dealt with in detail by Thomson.

The other assumption of Donnan, that the two phases do not become identical at the critical point, has not received sufficient consideration hitherto. It is well known that surface tension produces a hydrostatic pressure inside a spherical drop, in magnitude equal to $2T/r$, where T = surface tension and r = radius of drop. Apart from theoretical considerations, a glance at Fig. 2 will show that the liquid behind a convex surface must have a greater density than that bounded by a plane surface. The tube is full of liquid which is supported in the tube (neglecting the surface tension at the top) by the convex surface at the bottom. Since the liquid at the bottom is subjected to the hydrostatic pressure of the superincumbent liquid, it is compressed. This increase in density, negligible for ordinary curvatures, may become quite noticeable when the radius of curvature is small, as the following calculation shows:

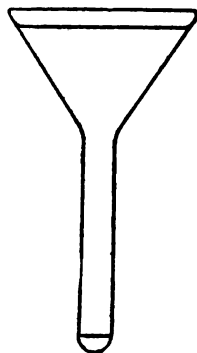


Fig. 2.

For water at ordinary temperature, surface tension = 70 dynes/cm.; compressibility = 4×10^{-11} in absolute units. So that the hydrostatic pressure inside a drop of 10^{-8} cm. radius would be 1.5×10^{-8} dynes/cm²., or about 150 atmospheres and the corresponding increase in density about 0.6%. For a radius¹ of 10^{-7} cm. on the pressure would be 1500 atmospheres and the increase in density 6%.

Thus the density of a liquid in the form of a small drop is greater than when it is bounded by a plane surface, and further, such physical properties of a liquid as solubility, vapor pressure and surface tension depend on the radius of the drop so that a small drop would not be identical with the vapor phase at a point, where the liquid, bounded by a

¹ Johannot (*Phil. Mag.*, 47, 501 (1899)) showed that stable films may be as thin as 6×10^{-7} cm.

plane surface and the vapor phase, become identical—which is just what Donnan has postulated.

Is it not more than likely that both these hypotheses present phases of the truth and that, as Smoluchowski has pointed out, local dense spots of varying volume and density are formed in a nearly saturated solution and that some of these, when once formed, are stable, for the reasons which Thomson and Donnan have given? As to the size of these drops, it seems possible, since it is related to the surface tension, that the size may vary with different liquids and also with the temperature for the same liquid. The amount of supersaturation possible is regulated by the size of these drops.

Summary.

1. The degrees of supersaturation of four solutions of liquids in water have been measured. In the cases of nitrobenzene and carbon disulfide, the existence of supersaturation has been definitely established.

2. The solubility of nitrobenzene in water has been measured at three different temperatures.

3. The solubility of water in nitrobenzene has been measured at six different temperatures.

4. Various important theories have been correlated and an attempt made to use them to explain the phenomena observed.

5. A change in the density and other physical properties of small drops with the radius has been suggested as fulfilling one of the conditions in Donnan's theory of the critical opalescence.

WINNIPEG, MANITOBA.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 103.]

THE CONDUCTANCE OF SOLUTIONS OF CERTAIN IODIDES IN ISOAMYL AND PROPYL ALCOHOLS.

By FREDERICK G. KEYES AND W. J. WINNINGHOFF.

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1. Introduction.

The study of the conductance of largely ionized solutes in aqueous solution has shown that the results over the range of concentration from 0.001 to 0.1 normal can be expressed fairly well by the equation $\frac{(c\gamma)^n}{c(1-\gamma)} = K$, first proposed by Storch.¹ In this expression c denotes the concentration, and γ the conductance ratio Λ/Λ_0 ; K is a constant, and n is another constant which has a value which varies somewhat with the nature of the solute, but almost always lies between 1.40 and 1.55.² In the case

¹ *Z. physik. Chem.*, 19, 13 (1896).

² Noyes, *THIS JOURNAL*, 30, 343 (1908).

of non-aqueous solutions a large amount of experimental material has been collected which seemed to show that electrolytes in these solvents obey a law very different from that applicable to aqueous solutions; thus in certain solvents the equivalent conductance has been found even to increase with increasing concentration. A satisfactory way of reconciling this discrepancy between the behavior of aqueous and certain non-aqueous solutions was recently described in an article published by Kraus and Bray,¹ in which it is shown that the conductance of almost any uniunivalent solute in any solvent from the concentration zero up to a fairly high concentration (one where the change in the viscosity of the solution becomes an important factor), can be expressed by an equation of the form

$$\frac{(c\gamma)^2}{c(1-\gamma)} = K + D(c\gamma)^m.$$

In this equation K , D , and m are empirical constants which vary with the nature of the solute and of the solvent and with the temperature. This expression evidently requires that any solute in any solvent conform to the mass-action law at sufficiently small concentrations (when the term $D(c\gamma)^m$ becomes negligible); and Kraus and Bray have shown that uniunivalent salts do in fact conform to this law at small concentrations in the solvent liquid ammonia, in which reliable conductance measurements have been made in very dilute solutions by Franklin and Kraus,² and also in certain alcoholic solvents which have been studied by Dutoit and Duperthuis.³ Computations made by Arrhenius⁴ have shown that the mass-action law is probably also conformed to by solutes in aqueous solution of salts at concentrations below 0.0002 normal.

It seemed nevertheless desirable to confirm and extend Dutoit's measurements with alcohols, as these were confined to a few concentrations and as they have recently been questioned by Walden.⁵ A study of the conductance of sodium iodide in isoamyl alcohol and in propyl alcohol and of ammonium iodide in isoamyl alcohol was therefore undertaken. As will be seen, the results of this investigation are in substantial agreement with those of Dutoit and Duperthuis.

This investigation was carried out with the aid of a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington, for which we wish to express our great indebtedness. We also wish to thank Prof. C. A. Kraus and Prof. A. A. Noyes for many helpful suggestions.

2. Preparation of the Substances and Solutions.

A good grade of isoamyl alcohol was fractionated repeatedly. The

¹ THIS JOURNAL, 35, 1315-1434 (1913).

² *Am. Chem. J.*, 23, 277 (1900).

³ *J. chim. phys.*, 6, 699 (1908).

⁴ *Meddelanden fr. k. Vetenskapsakademiens Nobelinstitut*, 2, No. 42, 1-12 (1913).

⁵ *Z. physik. Chem.*, 78, 257 (1911).

portion distilling between 130.5° and 131.5° was boiled with potassium hydroxide for several hours with a return-cooler. It was then distilled, metallic sodium was added to the distillate, and the alcohol was again distilled. By this treatment alcohol was obtained which had a specific conductance of 1.5×10^{-8} .

The pure alcohol was preserved in an amber-colored bottle from which the air was exhausted. Preserving the alcohol in this way lessened considerably the difficulties met with in the earlier part of the work, where yellow solutions of the iodides were obtained. The conductivity of these solutions also decreased rapidly, especially at the low concentrations. Treating the alcohol with potassium hydroxide as mentioned above removed this difficulty; but it was necessary to repeat this treatment frequently in order to keep the alcohol in good condition.

The propyl alcohol was dried with metallic sodium and fractionated, that portion distilling within the limits 97.3° and 97.5° being used for the measurements. This had a specific conductance of 2×10^{-8} . The propyl alcohol solutions also showed a slight tendency to become colored; but the change was very slow, and by carefully purifying the alcohol all trouble was avoided.

The sodium iodide was prepared by neutralizing purest sodium hydrocarbonate with gaseous hydrogen iodide; the ammonium iodide, by passing this gas into pure dry liquid ammonia. Very pure ammonium iodide was also obtained by subliming the commercial salt in a vacuum. Solutions of ammonium iodide prepared from the salt obtained by these two methods had identical conductances. All the salts were analyzed for their iodine content by precipitation of the iodine as silver iodide. The analyses in every case showed the theoretical amount of iodine within 0.1%. The hydrogen iodide was prepared according to a method described by Travers.¹

All the solutions were made as follows: The salt in the form of pellets, thoroughly dried in a vacuum at 150° , was weighed and placed in a weighed container; alcohol was quickly added, and the container was exhausted, sealed off, and again weighed. From the weight of salt and alcohol, the volume concentrations were calculated with the aid of density values. The density measurements, on account of the large coefficient of expansion of isoamyl alcohol, could not be conveniently made with the Ostwald-Sprengel type of pycnometer. A small narrow-neck flask of about 25 cc. capacity fitted with a ground glass stopper was found to give sufficiently accurate results and was accordingly employed.

The following table contains the values of the density measured at 25° and referred to that of water at 4° .

¹ Travers "Study of Gases," p. 51.

TABLE I.—DENSITY OF THE IODIDE SOLUTIONS AT 25°.

In isoamyl alcohol.			In propyl alcohol.		
Salt.	G. salt in 1000 g. solution.	Density.	Salt.	G. salt in 1000 g. solution.	Density.
None.....	0	0.8110	None	0	0.8043
NaI.....	35.80	0.8346	NaI	13.83	0.8141
NaI.....	84.96	0.8712	NaI	14.26	0.8141
NH ₄ I.....	0.845	0.8119	NaI	80.70	0.8626
NH ₄ I.....	23.41	0.8254	NaI	92.50	0.8715
NH ₄ I.....	32.34	0.8308	NaI	159.9	0.9256

3. Apparatus and Method of Measurement.

For the study of the conductance of non-aqueous solutions the methods hitherto employed are not well adapted, partly owing to the difficulty experienced in keeping the solutions free from moisture or other atmospheric impurities and partly owing to the oxidizing effect which the oxygen of the air may have upon organic liquids. Moreover, it is generally necessary to deal with small amounts of solvent, and consequently the method used must be such as will insure reasonable economy of material.

A new form of apparatus was therefore devised for the purpose. This is shown in Fig. 1. It consists of two parts, the cell proper M and the part N used for adding known amounts of solution to the solvent in the cell. The cell had a capacity of about 300 cc. The electrodes are shown at A, electrical connection being made with these through the small tubes B by means of mercury. The electrodes were made of bright platinum. Two different cells were used. In the larger cell the electrodes had an area of about 10 sq. cm. and were placed about $\frac{1}{2}$ cm. apart; in the smaller cell they had an area of about 1.5 sq. cm. and were placed about 1 cm. apart. Since it was necessary to shake the liquid in the cell, these electrodes were firmly tied together by means of glass crossbars connecting the corners. This gave reasonable assurance that the conductance capacity of the cell would not change during the measurements. However, this was measured frequently to make certain of this. The side tube C was merely for emptying the cell, and was sealed off before carrying out the measurements. The side tube at E was used in exhausting the cell, the opening at D being closed, either by the dropper N or by a rubber stopper. The cell was exhausted with a rotary oil vacuum pump capable of giving a pressure as low as 0.001 mm. After thoroughly exhausting it, the large stopcock, having a bore of 1 cm., could be closed and the cell handled at will.

The dropper N was a bulb of about 50 cc. capacity. The delivery tube L consists of a very fine capillary tube having a diameter of about 0.75 mm. This was further obstructed by a fine platinum wire. The dropper was closed at the top by the ground glass valve F. This valve was kept tightly closed by a piece of rubber tubing, as shown at H. The enlarge-

ment at G is part of a ground glass joint which fits into the cell M at D. The part shown at P is a small glass cap which fits on the end of the capillary tube. This was provided with four glass prongs. These served to catch the drops of liquid just before they fell. On falling from these tips they fell freely without touching the sides of the cell.

In addition to the cell just described, an apparatus was constructed for preserving liquids of low vapor pressure in a vacuum. This is shown in Fig. 2. The container is closed by the small valve *a*, which can be opened by raising the plug with an electromagnet acting on D. This was a flat piece of iron fixed in place in the glass tube by means of a little cement. The valve could be held open by suspending the plug, by means of the lugs *c*, from two small hooks attached at *d* (not shown in the figure). When closed the valve was tightly sealed by surrounding it with mercury from the reservoir B. In transferring solvent the cell could be sealed to the container at *f* and the whole apparatus exhausted through a side tube. The valve *a* could then be opened and the solvent distilled into the cell. The advantage of this container is that there are no stopcocks to contaminate the solvent with grease.

To make a measurement the cell was thoroughly dried, exhausted, and weighed. The required amount of alcohol (generally about 50 cc.) was then poured into the cell, and the cell was again exhausted and weighed, after which the conductivity of the solvent was immediately measured. The weighed dropper, in which was a solution of known concentration (by weight), was then placed in position, and the small space above the large stopcock was exhausted. The stopcock I was then closed and the large stopcock opened. By opening the valve F, solution varying from one to two drops to any desired volume could be added. The large stopcock was next closed and air was admitted to the chamber, after which the dropper was removed and

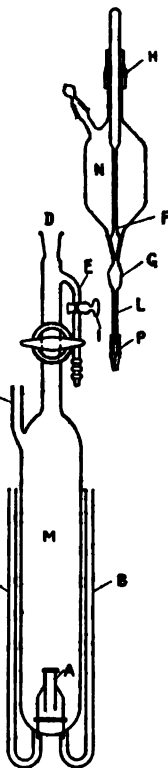


FIG. 1.

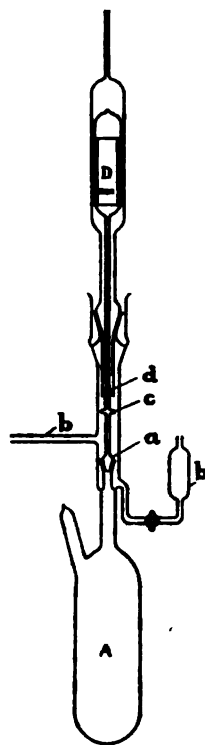


FIG. 2.

weighed. The solution in the cell was then thoroughly mixed and the conductance measured. This process could be repeated until the desired number of concentrations had been obtained. In this way solutions were easily and accurately made of any desired concentration up to the limit which could be measured in the cell.

The conductance-capacity of the cell was determined in the usual way, with the aid of a 0.005 normal potassium chloride solution.

The measurements were made with an ordinary slide-wire bridge provided with a platinum-iridium wire, which had been previously calibrated.

The conductance of the solvent, owing to its small value, could not be measured on the bridge. In order to obtain this value, the cell was attached directly to a 220-volt circuit and the current passing through the cell was measured. This was accomplished indirectly by measuring the voltage-drop across a shunt of 0.1 ohm, by means of the swing of a galvanometer. The galvanometer had previously been calibrated with the aid of a standard cadmium element in a circuit of 10,000 ohms resistance.

4. The Conductance Data.

The conductance data are presented in Tables II, III, and IV. They are given in the order in which they were originally obtained. Each series consists of six or more measurements which were all made with one filling

TABLE II.—CONDUCTANCE DATA FOR SODIUM IODIDE IN ISOAMYL ALCOHOL.

$10^4 c$.	$10^4 L$.	Λ .	$100\Lambda/\Lambda_0$.	$10^4 c$.	$10^4 L$.	Λ .	$100 \Lambda/\Lambda_0$.
0.00	7.79	100.00	55.12	74.36	1.33	17.11
0.0763	0.5306	6.96	89.35	73.28	94.67	1.29	16.59
0.2153	1.299	6.03	77.38	10.30	20.68	2.01	25.76
0.502	2.528	5.04	64.63	22.02	35.51	1.61	20.69
0.942	4.030	4.28	54.94	48.80	66.94	1.37	17.59
1.58	5.779	3.67	47.11	86.82	112.64	1.30	16.65
2.21	7.274	3.29	42.26	146.5	192.7	1.32	16.88
0.067	0.475	7.04	90.37	9.36	19.33	2.067	26.53
0.130	0.850	6.54	83.98	17.85	30.37	1.70	21.82
0.232	1.381	5.95	76.35	34.95	50.49	1.45	18.55
0.386	2.061	5.35	68.65	74.43	97.15	1.31	16.75
0.802	3.57	4.45	57.15	130.0	169.14	1.30	16.69
1.280	4.996	3.90	50.09	179.4	237.5	1.32	16.98
1.533	5.654	3.69	47.33	201.5	270.1	1.34	17.20
1.617	5.86	3.63	47.66	270.5	373.8	1.38	17.74
6.714	15.41	2.30	29.45	322.2	452.6	1.40	18.02
15.93	27.93	1.75	22.50	374.1	526.2	1.41	18.05
37.26	53.36	1.43	18.37	502.7	702.8	1.40	17.95
58.55	78.32	1.34	17.18	174.8	231.5	1.32	16.98
71.38	93.72	1.31	16.85	248.0	336.6	1.36	17.42
2.296	7.48	3.26	41.82	308.0	430.1	1.40	17.92
7.106	15.91	2.24	28.74	393.0	554.8	1.41	18.13
20.43	33.39	1.63	20.98	499.5	697.9	1.40	17.93
38.77	54.93	1.41	18.19				

TABLE III.—CONDUCTANCE DATA FOR AMMONIUM IODIDE IN ISOAMYL ALCOHOL.

$10^3 c$	$10^3 L$	Λ	$100 \Lambda/\Lambda_0$	$10^3 c$	$10^3 L$	Λ	$100 \Lambda/\Lambda_0$
0.00	7.92	100.00	2.290	7.994	3.49	44.06
0.0662	0.471	7.13	90.00	2.204	7.42	3.62	45.68
0.151	0.988	6.54	82.56	5.97	15.40	2.58	32.57
0.366	2.035	5.56	70.18	12.70	25.67	2.02	25.50
0.904	4.073	4.51	56.88	27.23	45.07	1.65	20.88
1.54	5.976	3.88	48.95	50.28	73.07	1.45	18.34
2.11	7.446	3.53	44.54	71.05	98.48	1.39	17.50
0.0575	0.4204	7.32	92.35	3.23	10.13	3.13	39.54
0.1707	1.099	6.440	81.29	6.57	16.39	2.49	31.48
0.3043	1.752	5.76	72.65	13.81	27.47	1.99	25.10
0.7909	3.679	4.650	58.70	29.75	48.17	1.62	20.42
1.39	5.583	4.015	50.68	47.27	71.34	1.46	18.44
1.81	6.713	3.714	46.88	67.35	94.10	1.40	17.63
0.051	0.377	7.47	94.30	62.88	87.93	1.397	17.63
0.117	0.800	6.87	86.72	88.35	118.8	1.346	16.99
0.263	1.556	5.94	74.98	112.7	150.2	1.332	16.81
0.644	3.180	4.94	62.36	137.0	182.8	1.335	16.85
1.365	5.520	4.04	51.00	171.7	229.6	1.337	16.88
2.208	7.720	3.49	44.09	58.08	82.03	1.412	17.82
0.0577	0.4286	7.43	93.79	81.30	110.2	1.356	17.12
0.1316	0.8947	6.80	85.79	102.6	137.1	1.336	16.87
0.2617	1.598	6.11	77.13	127.9	169.7	1.326	16.74
0.6980	3.395	4.87	61.41	161.8	215.9	1.334	16.84
1.376	5.567	4.05	51.06				

TABLE IV.—CONDUCTANCE DATA FOR SODIUM IODIDE IN PROPYL ALCOHOL.

$10^3 c$	$10^3 L$	Λ	$100 \Lambda/\Lambda_0$	$10^3 c$	$10^3 L$	Λ	$100 \Lambda/\Lambda_0$
0.00	20.10	100	53.40	448.6	8.40	41.8
0.0447	0.9057	20.25	...	75.08	585.2	7.79	38.7
0.1693	3.26	19.26	95.8	2.303	35.57	15.42	76.7
0.4553	8.276	18.17	90.4	5.092	69.28	13.61	67.7
1.074	18.12	16.87	83.9	12.37	141.65	11.44	56.9
2.083	32.57	15.62	77.7	29.81	283.6	9.510	47.3
0.0623	1.244	19.94	99.2	53.85	451.4	8.38	41.7
0.1581	3.060	19.36	96.3	77.45	601.9	7.77	38.6
0.2261	4.311	19.06	94.8	28.53	272.6	9.55	47.5
0.3902	7.167	18.36	91.3	55.4	459.2	8.29	41.2
0.6591	11.69	17.72	88.2	106.1	767.0	7.23	36.0
1.055	17.90	16.96	84.4	187.6	1219.5	6.5	32.3
1.498	24.41	16.30	81.1	315.6	1872.0	5.93	29.5
2.260	35.04	15.5	77.1	35.18	321.1	9.14	45.4
2.310	35.61	15.40	76.7	129.7	903.4	6.97	34.8
5.89	77.93	13.23	65.8	242.9	1506.5	6.21	30.9
13.26	149.7	11.28	56.1	362.0	2108.0	5.82	28.9
27.77	272.6	9.815	48.8				

of the cell. In the first column the concentrations $10^3 c$ are given expressed in milliequivalents of salt per liter of solution. In the second column are

given the specific conductance L , expressed in reciprocal ohms and multiplied by 10^6 . In the next column are given the equivalent conductances Λ expressed in reciprocal ohms; and in the last column are given the conductance-ratios Λ/Λ_0 multiplied by 100.

5. Treatment of the Results.

If the mass-action law is conformed to in dilute solutions, the equation $c\Lambda = (1/\Lambda) K\Lambda_0^2 - K\Lambda_0$ holds true, and a straight line would be obtained by plotting $1/\Lambda$ against $c\Lambda$. Extrapolation to zero concentration would then give the value of $1/\Lambda_0$. From this value of Λ_0 that of K can be calculated directly from the above equation by introducing known values of c and Λ , or it can be obtained by determining the slope of the line on the plot.

Plots made in this way showed that the mass-action law is conformed to in very dilute solution; for up to an ion-concentration about 0.0004 normal the points fall nearly on a straight line. Thus in the case of ammonium iodide in isoamyl alcohol the average deviation from the best representative straight line of the twelve points corresponding to the values of $1/\Lambda$ determined between the ion concentrations 0.00005 and 0.0004 is 0.8%; and in the case of sodium iodide in isoamyl alcohol the average deviations of the corresponding ten points is 0.4%. A plot showing these results is presented in Fig. 3. The results with sodium iodide in propyl

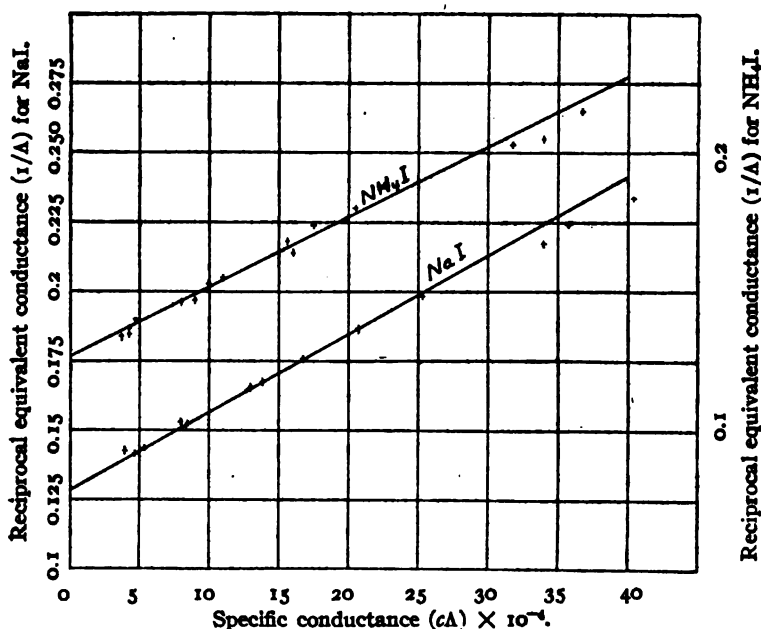


Fig. 3.

alcohol show a correspondingly good agreement with the mass-action law: when plotted, only the two measurements at the two lowest concentrations (45 and 62×10^{-6} normal) show an appreciable deviation from the best representative straight line.

The Δ_0 values obtained from such plots¹ are given at the beginning of Tables II, III and IV. The value given for ammonium iodide is only approximate.² The value for sodium iodide (7.79) is somewhat lower than the value (7.87) found by interpolation from Dutoit's results.

By transposing the Kraus equation and taking the logarithm of both sides we get the equation $\log \left(\frac{c\gamma^2}{1-\gamma} - K \right) = m \log c\gamma + \log D$. Hence, a straight line should be obtained by plotting the first member of this equation as ordinates against $\log c\gamma$ as abscissas, and the slope of this line should give m and its intersection with the axis of ordinates $\log D$.

Plots made in this way (with the aid of a provisional value of K derived from the dilute-solution plots referred to above) showed a very good agreement with the Kraus equation, especially in the more concentrated solutions. Variations in the dilute solutions were to be expected, since the equation is so sensitive in this region to the value assumed for K . Having determined from such plots the value of the constant m , the constants D and K were more accurately determined by plotting $c\gamma^2/(1-\gamma)$ against $(c\gamma)^m$. For the equation $c\gamma^2/(1-\gamma) = K + D(c\gamma)^m$ requires that this graph should be a straight line, the slope of which corresponds to the value of D and its intersection on the axis of ordinates to the value of K . Using this new value of K in a logarithmic plot of the kind first described, new values of m and D were obtained.

The final values of the constants so computed are given in Table V.

TABLE V.—CONSTANTS OF THE KRAUS EQUATION.

Alcohol.	Salt.	Δ_0 .	$10^4 K$.	m .	D .
Isoamyl.....	NaI	7.79	5.85	1.2	0.374
Isoamyl.....	NH ₄ I	8.00	6.93	1.17	0.324
Propyl.....	NaI	20.10	38.3	0.75	0.208

¹ Walden (*Z. physik. Chem.*, 78, 257 (1911)) has taken exception to this method of determining Δ_0 , involving the assumption that the mass-action law is obeyed in dilute solution, and has attempted to show that Δ_0 is better determined by using the Kohlrausch extrapolation formula. This, however, is a purely empirical relation, and in view of the present facts its use hardly seems to be justified.

² This value is in fact about 1% higher than the value (7.92) obtained by extrapolation on the dilute-solution plot. The reasons for the choice of this value were that variations took place in the cell-constant during the measurement of the dilute solutions which made the extrapolation somewhat uncertain and that this value fitted the results in concentrated solutions much more accurately than the extrapolated value. In other words, the Δ_0 value was really obtained by extrapolation from the concentrated solutions.

In Table VI are given side by side the "observed" equivalent conductance values accurately interpolated on a large-scale plot of Λ against $\log c$ and the "calculated" equivalent conductance values computed by the Kraus equation $c\gamma^2/(1 - \gamma) = K + D(c\gamma)^m$ with the aid of the constants given in Table V. The column heading $10^3 c$ gives the concentration in milliequivalents of salt per liter of solution.

TABLE VI.—OBSERVED AND CALCULATED VALUES OF THE EQUIVALENT CONDUCTANCE.

$10^3 c$.	NaI in isoamyl alcohol.			NH ₄ I in isoamyl alcohol.			NaI in propyl alcohol.		
	A obs.	A calc.	% diff.	A obs.	A calc.	% diff.	A obs.	A calc.	% diff.
0.00	7.79	7.92	20.10
0.05	7.182	7.194	+0.17	7.396	7.476	+1.08	(20.11)
0.10	6.636	6.658	+0.33	7.032	7.105	+1.04	19.65	19.53	-0.61
0.20	6.115	6.142	+0.43	6.256	6.352	+1.54	19.17	19.13	-0.21
0.40	5.307	5.335	+0.53	5.464	5.598	+2.46	18.42	18.49	+0.38
0.80	4.451	4.460	+0.20	4.672	4.794	+2.62	17.38	17.56	+1.03
1.00	4.184	4.183	-0.03	4.408	4.542	+3.03	17.00	17.21	+1.24
2.0	3.394	3.374	-0.61	3.588	3.663	+2.23	15.73	16.03	+1.90
5.0	2.560	2.534	-1.02	2.656	2.676	+0.75	13.62	13.56	-0.44
10.0	2.024	1.995	-1.43	2.168	2.164	-0.186	12.04	11.80	-1.99
20.0	1.649	1.635	-0.69	1.776	1.763	-0.73	10.44	10.31	-1.25
40.0	1.408	1.404	-0.28	1.448	1.456	+0.55	8.90	8.82	-0.90
100	1.294	1.290	-0.31	1.336	1.339	+0.22	7.33	7.26	-0.95
150	1.312	1.309	+0.023	1.332	1.335	+0.22	6.85	6.79	-0.88
200	1.339	1.336	-0.22						
300	1.393	1.400	+0.50						
400	1.413	1.459	+3.20						
500	1.396						

It will be seen that the agreement of the observed values with those calculated by the Kraus equation is fairly close (except at the highest concentration in the case of sodium iodide in isoamyl alcohol) concentration.

6. Summary.

In this article has been described an accurate method of determining conductances in an evacuated apparatus.

Results have been presented on the equivalent conductance of sodium iodide and ammonium iodide in isoamyl alcohol and of sodium iodide in propyl alcohol from a concentration of about 0.0005 normal up to saturation (about 0.5, 0.2, and 0.4 normal), respectively.

It has been shown that up to an ion concentration of 0.0004 normal these electrolytes conform to the mass-action law; and that their conductance is expressed throughout the whole range of concentration by the equation $c\gamma^2/(1 - \gamma) = K + D(c\gamma)^m$ proposed by Kraus, in which c is the concentration, γ is the conductance-ratio Λ/Λ_0 , and K , D , and m are empirical constants. Thus the corresponding generalizations drawn by Kraus and Bray are confirmed by these results.

Boston, April, 1916.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON.]

THE DISSOCIATION OF FERRIC OXIDE IN AIR.¹

By J. C. HOSTETTER AND R. B. SOSMAN.

Received May 1, 1916.

In a paper which appeared in the April number of *THIS JOURNAL*,² the authors showed by measurements of dissociation pressure that ferric oxide (Fe_2O_3) and magnetite (Fe_3O_4) form a continuous series of solid solutions from Fe_2O_3 to Fe_3O_4 , or at least to a point very near Fe_3O_4 .

The form of the dissociation-pressure curves at 1100° and 1200° near the composition of pure Fe_2O_3 offers special interest. These curves rise

Minerals:

M = Magnetite

H = Hematite

Martite (pseudomorphs)

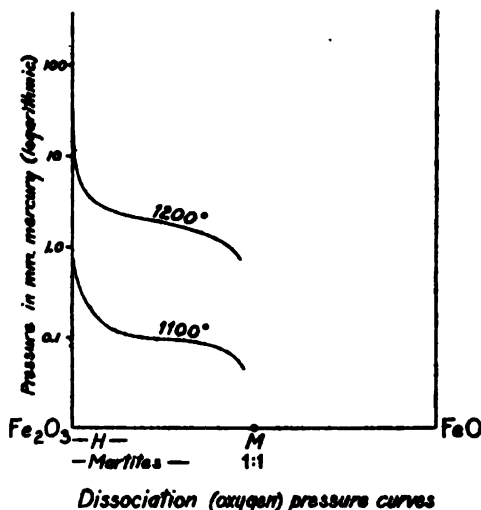


Fig. 1.—Pressure-composition isotherms of the system Fe_2O_3 - Fe_3O_4 .

rapidly as the percentage of FeO approaches zero, as if to become asymptotic to the axis of ordinates (see Fig. 1). The form of the curves led us to suggest³ an explanation of an observation made by Baxter and Hoover during their work on the atomic weight of iron.⁴ These investigators found that there was a constant difference in weight, amounting to about 0.2 mg. in 5 g., or 0.004%, between Fe_2O_3 heated in a current of air and the same oxide heated in a current of oxygen; the temperature was not measured but was estimated to be in the neighborhood of 1100° . The oxygen value was the higher, and the atomic weight of iron derived therefrom agreed closely with that obtained from FeBr_3 . Baxter and Hoover, however, very naturally hesitated to believe that there could be any dissociation of Fe_2O_3 at 1100° under a pressure of 152 mm. of oxygen, since Walden's results⁵ had shown that Fe_3O_4 is formed in air only above 1350° ; they, therefore, ascribed the higher weight in pure oxygen to occlusion of a small quantity of this gas.

¹ Presented at the Urbana meeting of the Society, April 18, 1916.

² *THIS JOURNAL*, 38, 807-833 (1916).

³ *Loc. cit.*, p. 828.

⁴ *THIS JOURNAL*, 34, 1657-1669 (1912).

⁵ *Ibid.*, 30, 1350-1355 (1908).

If the difference in weight between ignitions in air and in oxygen is due to occlusion of oxygen, then as the temperature is raised the difference should either be constant or should decrease, since it is very unlikely that the amount of occluded oxygen would be greater at high temperatures than at low temperatures. If, on the other hand, the difference is due to true dissociation, it is to be expected that the slope of the curves of dissociation pressure against composition (at constant temperature) between 152 and 760 mm. of oxygen will increase with the temperature, and that the difference in weight between oxygen and air ignitions will, therefore, also increase with the temperature.¹ This point seemed more easily susceptible of proof than it turned out to be, but the results which follow show clearly that a small but appreciable amount of dissociation of Fe_2O_3 does occur in air at temperatures above 1000° .

Materials.—Ferric oxide from pure electrolytic iron through the nitrate, and Kahlbaum's purest ferric oxide, were used in the experiments described below.² The oxygen was the commercial product supplied in cylinders.³ It was purified by passing through a train containing, in the order named, soda-lime, calcium chloride, sulfuric and chromic acid, soda-lime, calcium chloride, copper oxide at $650\text{--}700^\circ$, potassium hydroxide which had been fused with permanganate, and phosphorus pentoxide. The air was also taken from a tank, and was purified through the same train. The line contained no stopcocks, and all joints were either sealed glass or Wood's metal joints, so that there was no chance of contamination of the gas current by reducing vapors from lubricated joints or stopcocks.

Apparatus.—A horizontal tube furnace was used, made of platinum wire wound on an alundum furnace core. The arrangement of the ignition tube is shown in section in Fig. 2. The central tube was at first of fused silica, later of Haldenwanger porcelain, 20 mm. inside and 25 mm. outside diameter. This was connected at one end to a fused silica tube by means of a water-cooled brass sleeve and Wood's metal fillings. The brass sleeve had a side tube for the admission of oxygen or air. The end of the silica tube was closed by a brass sleeve with a screw cap, in which was a smaller brass bushing large enough for a 1 mm. platinum wire.

¹ It is assumed that the oxide is cooled rapidly enough to avoid reoxidation as the temperature falls. This was accomplished in our experiments by withdrawing the boat quickly into a water-cooled silica tube. The rate of reoxidation is, however, so slow that cooling the boat in the furnace itself by merely shutting off the current will produce differences of weight between air and oxygen ignitions.

² These oxides have been described in our previous paper (p. 811). The oxide from electrolytic iron used here was not, as there described, made directly from the first nitrate, but from a recrystallized nitrate.

³ Manufactured by the Linde Air Products Company. Baxter and Hoover also used Linde oxygen.

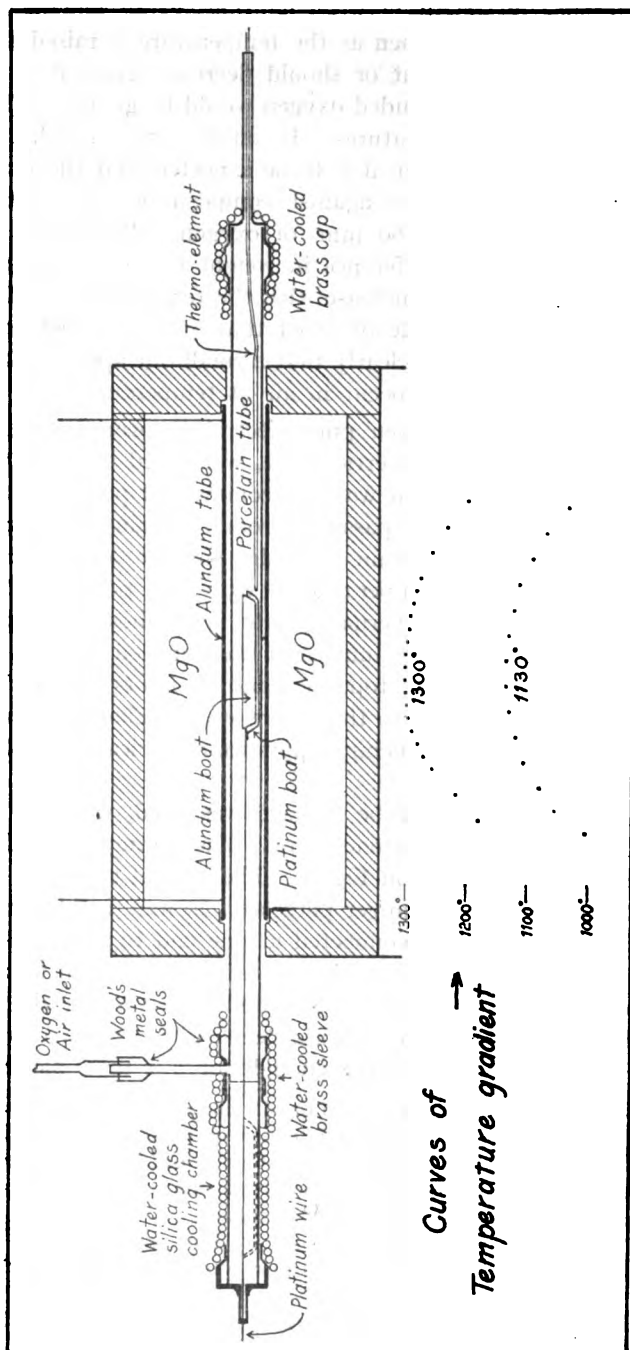


Fig. 2.—Apparatus for experimental ignition of ferric oxide in air and in oxygen.

At the opposite end of the furnace the porcelain tube was closed by a water-cooled brass cap through which entered the platinum-platinrhodium thermoelement.

Both platinum and alundum boats were used. Further details concerning these will be contained in the experimental results.

Weighings were made on an Ainsworth type QA analytical balance adjusted to a sensibility of 0.01 mg. By controlling the atmosphere within the balance by means of caustic potash, and taking weighings at measured intervals after removal from the desiccator, it was found possible to obtain results reproducible to 0.02 mg. in 10–15 g., including all the variations possible in igniting and handling the boat.

The temperature gradient of the furnace tube was explored by means of a thermoelement. At 1300° the temperature was uniform within 15° over the length of the boat, which was 100 mm. long.

Procedure.—The furnace was first heated to a definite constant temperature, with the boat and charge standing in the silica cooling chamber and oxygen or air passing. When constant conditions were attained, the boat was pushed into place in the center of the furnace by means of a platinum wire. At the end of the heating, the boat was rapidly withdrawn by means of the wire to the water-cooled silica cooling chamber, from which it was transferred when completely cooled to a desiccator containing phosphorus pentoxide.

Constancy of Weight of Platinum.—For the first experiments a boat of pure platinum was used, as in the work of Baxter and Hoover. When heated alone in oxygen and in air, the boat lost very little weight, much less than was to be expected from the results of the experiments of Burgess and Sale.¹

In the presence of iron oxide, however, a decidedly different result was obtained. Two different effects are distinguishable: (1) At a temperature of 1200° or higher, the platinum reacts with the ferric oxide, absorbing iron and giving off oxygen;² the net result is a loss in total weight, but a gain in the weight of the boat as determined after removing the oxide and cleaning the boat in hydrochloric acid. (2) Below 1200° there is still a continuous loss in total weight, though less than at higher temperatures; but the weight of the boat alone shows an equivalent loss. In other words, the ferric oxide, while remaining constant in weight, seems to have acted as a catalyzer for the oxidation of the platinum by gaseous oxygen.

The summarized records of the heatings and the changes in weight of the boat are presented in Table I. In nearly all cases the loss of the boat when containing Fe_2O_3 is very much greater than its loss alone. The only

¹ *J. Ind. Eng. Chem.*, 7, 561–564 (1915); *Bull. Bur. Standards*, 12, 289–316 (1915).

² Sosman and Hostetter, *J. Wash. Acad. Sci.*, 5, 293–303 (1915).

exception is the set of two heatings covering 34 hours which gave a loss of only 0.04 mg.; in this case, however, over half of the heating was at 1000° , and the heatings were made in a current of air, both conditions being unfavorable for oxidation of platinum. A part of the losses after heating with Fe_2O_3 must undoubtedly be ascribed to solution of platinum by hot dilute HCl , in which the boat was allowed to stand for about one minute in order to remove adhering powder of Fe_2O_3 . The loss so caused must have been very small, however, because standing half an hour in concentrated HCl , which in the presence of air is known to dissolve platinum, removed only 0.10 mg.

TABLE I.

Number of heatings.	Time, hours.	Gas.	Temperature.	Boat contained.	Wt., mg.	Change of wt., mg.
0	0	13158.60
6	30.9	Air and oxygen	$1050-1100^{\circ}$	Fe_2O_3	13156.88	-1.72
1	5.0	Air	1150°	Fe_2O_3	13154.41 ¹
4	17.5	Air	$1140-1230^{\circ}$	Fe_2O_3	13155.25	+1.11
7	33.6	Air and oxygen	$1075-1105^{\circ}$	Fe_2O_3	13154.45	-0.80
1	5.0	Oxygen	1100°	No charge	13154.40	-0.05
1	5.0	Air	1100°	No charge	13154.30	-0.10
1	16.25	Oxygen	1100°	No charge	13154.49 ²
					13154.43	-0.06
3	36.5	Oxygen	1100°	Fe_2O_3	13150.14	-4.29
					13150.04	-0.10 ³
2	34.0	Air	$1100-1000^{\circ}$	Fe_2O_3	13150.00	-0.04
4	42.0	Oxygen	$1050-1100^{\circ}$	Fe_2O_3	13149.18	-0.82

It is conceivable that heating for a long time in oxygen might put the surface of the platinum in a condition to be more easily attacked by dilute HCl . To test this, the platinum boat in which the various alundum series were heated (see following section), which had been exposed to oxygen and air at temperatures of $1100-1300^{\circ}$ for a total of 573 hours, was treated with hot dilute HCl in the usual manner. It lost 0.30 mg., and on a second treatment 0.11 mg. Even after this long heating, therefore, the loss caused by the HCl treatment is considerably less than the losses produced in a few hours by heating in contact with Fe_2O_3 .

The average loss of weight per hour of the boat heated alone, as calculated from the figures of Table I, is 0.006 mg.; the average loss per hour when heated in contact with Fe_2O_3 is 0.043, or seven times as great. There is certainly a decided difference in the effect of the two sets of conditions, which seems best explained by assuming a catalytic action of Fe_2O_3 on the reaction between platinum and oxygen. This catalytic effect of ferric oxide on certain oxidation reactions has long been known. Its effect

¹ Boat accidentally amalgamated. Cleaned in HNO_3 and HCl .

² New set weights.

³ Stood 30 min. in conc. HCl .

on the oxidation of sulfur dioxide by oxygen is, perhaps, the most familiar.

In the hope of getting a boat that would be more constant in weight, we obtained from the American Platinum Works a boat made of an alloy containing 4% of rhodium. This lost weight, when heated alone, even more rapidly than the old boat. The figures are given in Table II.

TABLE II.
Loss of Weight of Boat Containing 4% Rhodium.

Treatment.	Wt., mg.	Loss, mg.	Loss per hour, mg.
Original weight.....	16774.45
Heated 17.0 hours, in oxygen, at 1100° with basic ferric nitrate in boat.....	16768.89	5.56	0.33
Heated alone 3.0 hours, in oxygen, at 1100°..	16768.49	0.40	0.13
Heated alone 3.0 hours, in oxygen, at 1100°..	16768.24	0.25	0.08

The result must not be taken as an indication that the presence of rhodium increased the rate of loss. This particular boat was made after the European war had cut off the supply of pure platinum and rhodium, and probably contained a little iridium, indications of which were seen on the thermoelement tubes. Iridium is known to be considerably more volatile than platinum or rhodium, and its presence would cause a greater rate of loss from the platinum-rhodium boat.

Constancy of Weight of Alundum Boats.—Alundum gave much more satisfactory results at all temperatures than did platinum. It is almost absolutely constant in weight at 1200° and lower. This is not surprising, when it is considered that alumina is a fully saturated oxide, while platinum is an oxidizable metal.

The so-called "alundum" boats are made of fused pure alumina, bonded together by a vitrified silicious bond. The boats which we used were of the composition designated as "RA 84." Above 1200° they lost weight at a uniform rate, probably because of volatilization of alkali or silica from the bonding material. The changes in weight of an alundum boat are shown in Fig. 3. To prevent the loss of small particles, which we found were scraped off when the unprotected boat was dragged through the furnace tube, the boat was placed inside of a platinum boat, from which it was removed for weighing. At 1300°, the highest temperature used, the alundum showed no sign of sticking to the platinum, and it seemed to lose no weight through abrasion in handling.

To test the effect of the binding material on the loss of weight, we made several ignitions on a boat made of the mixture "RA 98," which is more porous and contains less binder than "RA 84." The loss was decidedly less at 1300°, but was still measurable at 1200°. The results on alundum are contained in Table III.

The question of a possible reaction between ferric oxide and the material of the boat must also be considered. At 1200° no evidence of reaction

could be found. At 1300° , the highest temperature used, microscopic examination showed that a trace of Fe_2O_3 had been taken up by the

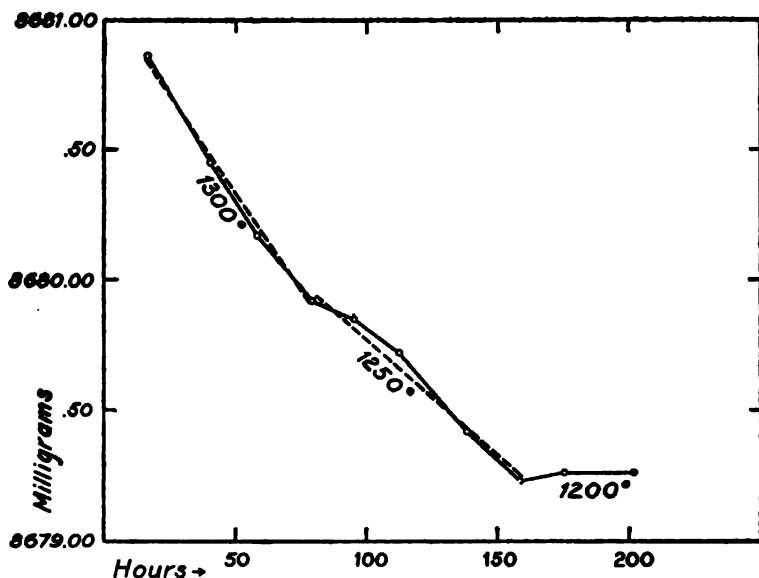


Fig. 3.—Changes in weight of alundum boat of composition "RA 84" heated in oxygen.

vitreous binder of the boat, but that no reaction had occurred with the fused alumina.

TABLE III.				
Loss of Weight of Alundum Boats Heated in Oxygen.				
Temperature.	Time, hours.	Wt., mg.	Change, mg.	Change per hour, mg.
RA 84				
1300°	16.5	8680.86	..	-0.015
1300°	23.0	8680.45	-0.41	
1300°	19.1	8680.17	-0.28	
1300°	20.9	8679.92	-0.25	
1250°	16.0	8679.85	-0.07	-0.009
1250°	17.4	8679.72	-0.13	
1250°	26.0	8679.42	-0.30	
1250°	20.5	8679.23	-0.19	
1200°	16.9	8679.26	+0.03	+0.001
1200°	26.8	8679.26	0.00	
RA 98				
1200°	17.5	6690.12	..	-0.004
1200°	52.7	6689.90	-0.22	
1300°	18.2	6689.80	-0.10	-0.009
1300°	19.8	6689.56	-0.24	

Dissociation of Fe_2O_3 .—On account of the changes in weight of platinum in contact with Fe_2O_3 , the results obtained with the platinum boat

were not entirely satisfactory. A difference in weight between air and oxygen ignitions was clearly shown, however, as will appear from Fig. 4. The curve represents the changes in weight at 1100° of ferric oxide made from nitrate (electrolytic iron) after correction for the change in weight

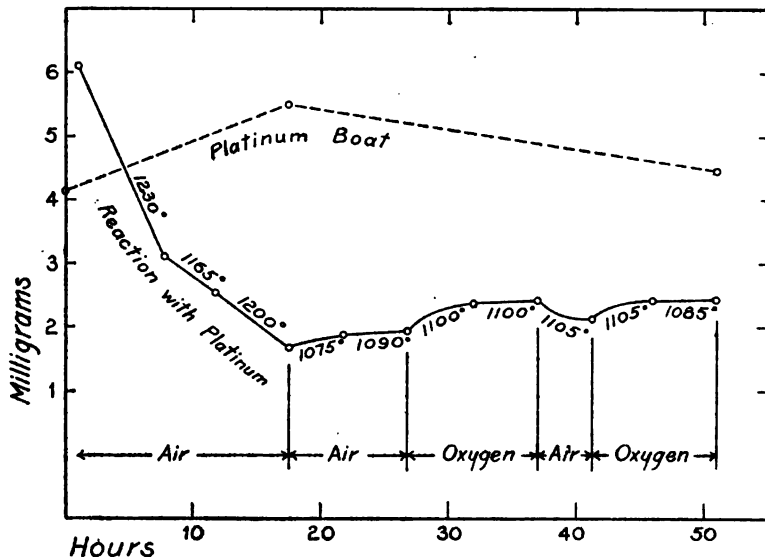


Fig. 4.—Changes in weight of ferric oxide heated in a platinum boat in air and in oxygen.

of the platinum boat. To eliminate the small losses caused by removal of the oxide from the boat, which was done twice during the series, the weights are all referred to a common basis. The original weight of oxide was 12.196 g., and the weight of the boat 13.154 g.

The series made in the alundum boat is plotted in Fig. 5. The boat weights were corrected according to the rates of loss shown in Fig. 3, and were then deducted from the total weights as determined, to give the data plotted in Fig. 5. Kahlbaum's oxide was used.

It will be evident from the curves of Fig. 5 that a prompt change of weight follows each change from air to oxygen or back again, the weights in air being lower than those in oxygen. Furthermore, the difference between air and oxygen is greater at the higher temperatures than at the lower. This indicates that the differences in weight are due not to adsorption of oxygen at the higher oxygen pressure, but to a small amount of dissociation of Fe_2O_3 in air.

Coincident with the series of weight changes there occurs a gradual increase in the total weight of the oxide. This must come from the sublimation of some substance on to the oxide charge, possibly platinum, or alkali or silica from the porcelain tube. This steady gain in weight,

independent of the dissociation and re-oxidation, was confirmed by another series made at 1100–1200° in oxygen in an alundum boat, with a new charge of Kahlbaum's oxide. As shown in Table IV there was a steady, though very small, gain in weight. The total gain, after an initial loss

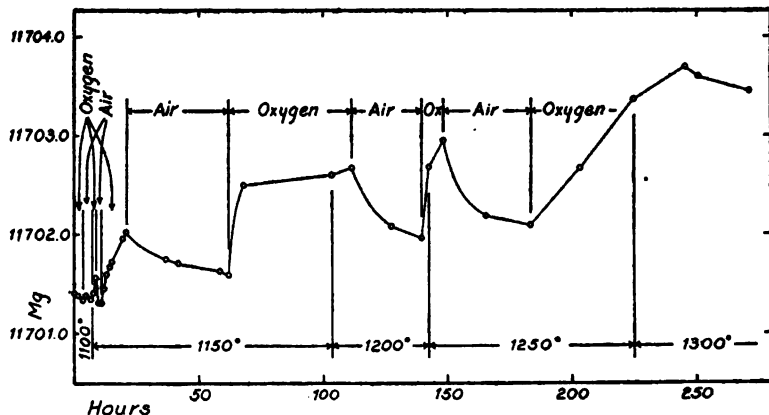


Fig. 5.—Changes in weight of ferric oxide heated in an alundum boat in air and in oxygen.

due to moisture, was 2.00 mg. on 10.605 g. Fe_2O_3 , or 0.019%; a gain of 0.010%, part of which may have occurred during the initial heating, could have resulted from the oxidation of 0.09% FeO which is present in the original oxide.

This slow gain undoubtedly masks at 1100–1200° the small decrease of weight of the oxide in oxygen which should occur with rising temperature in the series of Fig. 5, if the dissociation curve really has the form of an asymptote to the pressure axis. At 1300°, however, at the end of the curve of Fig. 5, a loss of weight in oxygen is observed which may represent the beginning of an appreciable dissociation even at 760 mm. oxygen pressure.

TABLE IV.
Kahlbaum's Ferric Oxide Heated in Oxygen in Alundum Boat.

Temperature.	Total time, hours.	Wt. boat and Fe_2O_3 , mg.	Temperature.	Total time, hours.	Wt. boat and Fe_2O_3 , mg.
...	0	19283.03	1200°	66.1	19283.65
1150°	16.9	19282.47	1200°	85.9	19283.83
1150°	22.2	19282.66	1200°	109.3	19284.36
1150°	41.7	19282.88	1200°	127.8	19284.47

Not many cases have been studied of this type of dissociation, in which only one of the two components is volatile, and in which a solid solution is left behind by the escape of the volatile component. One which was mentioned in our previous article is the system $\text{CoCl}_2 \cdot 6\text{NH}_3$ – $\text{CoCl}_2 \cdot 2\text{NH}_3$.¹ The

¹ Biltz and Fetkenheuer, *Z. anorg. Chem.*, 89, 106 (1914).

dissociation-pressure isotherm of this system may be interpreted in exactly the same manner as our Fe_2O_3 - Fe_3O_4 system, and it is quite possible that additional measurements nearer the composition of pure $\text{CoCl}_2 \cdot 6\text{NH}_3$ than those made by the authors referred to would show a similar "asymptotic" curve.

A theoretical extension of our interpretation of the dissociation pressure curve seems to fit in with Langmuir's work¹ on the adsorption of gases by solid surfaces. It appears probable that the atoms of an adsorbed gas are really in direct chemical combination with the atoms in the surface of the adsorbing solid; these surface atoms, by reason of their position, are in a chemical state which is somewhat different from that of the atoms within the body of the solid. The oxygen atoms adsorbed on the surface of a small crystal of ferric oxide may, therefore, be considered as chemically combined, and their chemical environment is not essentially different from that of the oxygen atoms just within the bounding "surface" of the crystal, for this surface itself, as the X-ray analysis of crystal structure shows, is only a layer of iron and oxygen atoms spaced according to some uniform plan. If Maxwell's demon were sitting in the midst of a group of small ferric oxide crystals which held some oxygen adsorbed, and if he were counting the oxygen atoms which escaped as the temperature was raised, it might be difficult or impossible for him to say when the adsorbed oxygen had all been given off, and true dissociation had begun. The essential continuity of the two kinds of combination of oxygen may be expressed by drawing our dissociation-pressure curve as in Fig. 6.

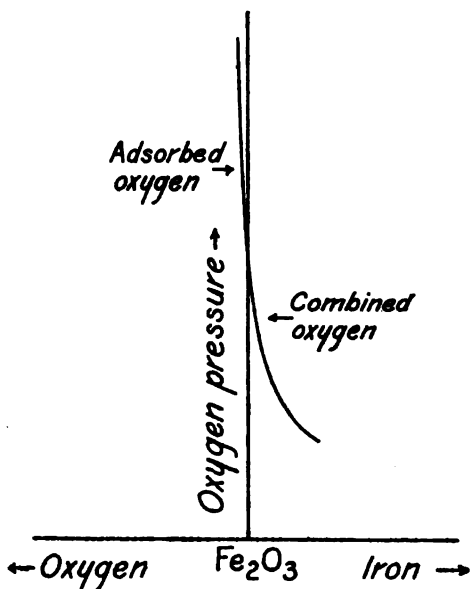


Fig. 6.—A theoretical interpretation of the form of the curve of dissociation-pressure against composition for compositions near ferric oxide.

The great ease of dissociation of the first small fraction of a per cent. of the oxygen of Fe_2O_3 serves to account for the fact that out of 75 or more iron oxides, natural and artificial, which we have analyzed in this laboratory, only one failed to show a determinable amount of ferrous iron.

¹ THIS JOURNAL, 37, 1139-1167 (1915); *Phys. Rev.*, 6, 79-80 (1915).

Summary.

Previous work by the authors has shown that Fe_2O_3 dissociates to form a solid solution of Fe_3O_4 in Fe_2O_3 , and that the curve of dissociation pressure against composition at a given temperature rises rapidly as the composition approaches pure Fe_2O_3 . The present experiments show that there is a measurable dissociation of Fe_2O_3 in air at all temperatures between 1100° and 1300° , and that the amount of dissociation increases with the temperature. This is shown by the increasing difference in weight between ignitions in air and in oxygen as the temperature is increased. The dissociation-pressure-composition curve thus takes the form of a curve asymptotic to the axis of ordinates, when the ordinates are pressures.

The best container for the Fe_2O_3 at 1100° and 1200° is alundum (bonded fused alumina) which is almost absolutely constant in weight at these temperatures, although it loses weight steadily at higher temperatures. The loss in weight of pure platinum at 1000 – 1200° is very small, but is considerably increased if the platinum is in contact with ferric oxide.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE.]

THE SEPARATION OF ERBIUM FROM YTTRIUM.

[PART I.]

BY P. S. WILLAND AND C. JAMES.

Received March 2, 1916.

The element erbium, or neocerium as it is sometimes termed, is very much rarer than was formerly supposed. Very small amounts, when mixed with yttrium, cause the precipitates and solutions to show a pink or rose color. Also, concentrated solutions of yttrium nitrate, containing very small quantities of erbium, show a strong absorption spectrum due to the latter element. During the last few years, practically no work has been done upon this substance apart from the researches of Hoffmann and Burger.¹ These investigators obtained erbium salts which, if not absolutely pure, are the purest yet known. They also claim that erbium is a simple definite element and not complex, as stated by Auer von Welsbach. This is entirely in agreement with the later work of one of the authors who has submitted erbium bromate to a very long series of fractionation without causing any change in the absorption spectrum. All differences observed were proved to be due to varying conditions of concentration, acids or acidity.

Fractional crystallization, so far, has failed to separate erbium from yttrium rapidly. This type of operation, when bromates or ethylsulfates are employed, quickly removes terbium, dysprosium and holmium in the

¹ *Ber.*, 41, 308 (1908).

least soluble, while thulium, ytterbium and lutecium collect in the mother liquor.

In order to study the separation of erbium from yttrium systematically, it seemed necessary to start with two types of yttrium erbium oxide material, one in which yttrium was in excess, while the other consisted mainly of erbium. The results obtained should show whether selected methods will work with the same rapidity at both ends of the series, or whether it would be advisable to use two different ones.

The results obtained by using oxides containing an excess of yttrium are given in this paper which forms part one. Part two will appear at a later date.

Fractional Precipitation by Means of Sodium Phosphate.—Twelve grams of the oxides of yttrium and erbium were dissolved in dilute nitric acid, diluted to one liter, boiled and stirred with steam. A 10% solution of sodium phosphate was then added drop by drop from a separatory funnel. When sufficient of the precipitate had formed it was filtered off, and the process was repeated until four fractions had been taken. A concentrated solution of oxalic acid was then added to throw out what rare earths remained. The first four fractions were dissolved in a mixture of equal volumes of concentrated nitric acid and water, precipitated as oxalates and ignited to oxides. The fifth fraction was ignited, boiled with water to remove the sodium, filtered and well washed. The oxide was then dissolved in nitric acid and precipitated as the oxalate, and again ignited. The equivalents were then determined.

At. wt. of fraction.....	(1)109.2	(2)106.9	(3)104.1	(4)106.8	(5)98.9
Grams.....	1.01	0.34	0.56	0.67	8.77

Fractional Precipitation by Means of Potassium Ferrocyanide.—Ten grams of oxides were dissolved in about 140 cc. of formic acid, and diluted to about one liter. The liquid was boiled and stirred and a 10% solution of potassium ferrocyanide added drop by drop. The precipitate, which was somewhat colloidal, was easily separated by filtering through a paper mat. Three fractions were taken. The precipitates, which gradually turned blue, were dissolved in concentrated hydrochloric acid, and thrown down as oxalates. These oxalates upon ignition gave brownish oxides, which were dissolved in nitric acid and reprecipitated and ignited.

At. wt. of fraction.....	(1)102.0	(2)102.4	(3)97.7
Grams.....	1.25	3.94	3.66

Fractional Precipitation by Means of Sodium Nitrite.—Ten grams of oxides were dissolved in hydrochloric acid, diluted to one liter, boiled and stirred with steam. Sodium nitrite was gradually added until enough precipitate had formed. The precipitate was removed and the process repeated until five fractions were obtained. The sixth one was obtained by adding concentrated oxalic acid to the acidified liquid. In this last

case the oxide formed by igniting the oxalates was boiled with water to remove any sodium which might have been present. All the fractions were purified and the equivalents determined.

At. wt. of fraction	(1)115.9	(2)115.5	(3)109.1	(4)103.3	(5)101.8	(6)89.9
Grams.....	1.17	0.64	1.84	1.05	1.01	3.60

Fractional Precipitation by Means of Potassium Cobalticyanide.—Ten grams of oxides were dissolved in hydrochloric acid and diluted to one liter. A 10% solution of the cobalticyanide was slowly added to the boiling and well-stirred solution. Four fractions were taken in this manner, while the last fraction was formed by adding oxalic acid. The rare earth cobalticyanides were decomposed by boiling with sodium hydroxide. The resulting hydroxides were poured upon a filter, well washed with water, dissolved in hydrochloric acid and precipitated as oxalates. These oxalates were purified by several precipitations.

At. wt. of fraction.....	(1)112.2	(2)107.1	(3) ...	(4)100.3	(5)87.8
Grams.....	2.07	2.06	...	0.72	2.70

Fraction three was too small to work with. During the purification of the oxides a certain amount of the material was lost.

The potassium cobalticyanide was prepared in the following way: Potassium cyanide was added to a hot solution of cobalt chloride until no more cobalt cyanide was precipitated. The cyanide was filtered off, washed, dissolved in potassium cyanide, boiled and acetic acid gradually added. The crude cobalticyanide solution was then added to a strongly acid and boiling solution of copper chloride. The precipitated copper compound was removed by filtration, washed and boiled with potassium hydroxide. The copper oxide was separated and the yellow solution evaporated until crystals of the potassium salt were obtained upon cooling.

Fractional Crystallization of the Ammonium Double Sulfates.—About 10 g. of oxides were dissolved in hydrochloric acid, diluted, and an excess of ammonium sulfate crystals added. The solution was then evaporated upon the water bath, and three fractions taken. The fourth was obtained by the addition of oxalic acid.

The equivalents of the first and last fractions only were determined, since the method showed no fractionation.

At. wt. of fraction.....	(1)101.1	(4)101.3
Grams.....	1.95	1.12

Fractional Crystallization of the Diphenylmonosulfonates.—Three grams of oxides were dissolved in dilute hydrochloric acid and slightly diluted. The solution was heated to boiling and a solution of sodium diphenylmonosulfonate added. Upon cooling, scales of the diphenylsulfonates separated out. The process was repeated until four fractions had been taken. These were dissolved in large quantities of hot water and precipitated in the form of the oxalates, and ignited.

At. wt. of fraction.....	(1)98.5	(2)98.9	(3)100.3	(4)100.8
Grams.....	0.46	0.15	0.61	1.34

Crystallization of the Picrates.—Twenty grams of the oxides were dissolved in a slight excess of picric acid solution at 100°. The oxides dissolved very slowly. When the solution was complete, the liquid was allowed to cool and crystallize. The usual scheme for fractional crystallization was then followed for about ten series, keeping a maximum of five fractions. The picrates were then changed to oxalates and ignited to oxides.

At. wt. of fraction.....	(1)99.85	(2)100.00	(3)102.00	(4)102.15	(5)102.70
Grams.....	0.39	3.95	9.66	2.72	0.85

This work indicates that the erbium accumulates in the most soluble portion, which is the usual circumstance in fractional crystallization. This method of fractionation does not compare favorably with several of the well-known methods, since the separation of yttrium and erbium is so slow and the solution so dilute.

Fractional Precipitation by Means of Sodium Carbonate in the Presence of Ammonium Acetate.—About 10 g. of oxides were dissolved in dilute hydrochloric acid, the liquid diluted to about a liter, and 30 g. of ammonium acetate added. The solution was boiled, well stirred with steam, and precipitated with a 5% sodium carbonate solution. Four fractions were taken.

At. wt. of fraction.....	(1)106.9	(2)106.2	(3)104.95	(4)96.80
Grams.....	0.30	1.07	3.33	4.29

Fractional Precipitation by Means of Ammonium Oxalate in the Presence of Ammonium Acetate.—The method outlined above was followed in this case with the exception that ammonium oxalate was used in place of sodium carbonate.

At. wt. of fraction.....	(1)104.25	(2)103.35	(3)100.8	(4)97.65
Grams.....	2.12	2.07	2.99	2.29

Fractional Precipitation by Means of Ammonium Succinate in Presence of Ammonium Acetate.—This method was similar to the above with the exception that a 10% solution of ammonium succinate was used in place of a 5% ammonium oxalate. Five fractions were obtained.

The equivalents of the first and last fractions only were determined, since the method showed scarcely any separation.

At. wt. of fraction...	(1)101.05	(2) ...	(3) ...	(4) ...	(5)98.65
Grams.....	2.05	1.50	2.22	1.61	2.08

Fractional Precipitation by Means of Sodium Phosphate in the Presence of Ammonium Acetate.—The procedure in this case was similar to the foregoing with the exception that sodium phosphate was substituted for ammonium succinate. This time, however, four fractions were obtained. The equivalents of the first and last were determined.

At. wt. of fraction.....	(1)101.7	(2) ...	(3) ...	(4)98.2
Grams.....	0.96	2.56	2.66	3.18

Fractional Precipitation by Means of Sodium Hydroxide in the Presence of an Excess of Tartaric Acid.—Ten grams of oxide were dissolved in hydrochloric acid, diluted to a liter, and 40 g. of sodium potassium tartrate added. Sufficient acid was then added to dissolve the precipitate formed, and the whole boiled and stirred with steam. A 20% solution of sodium hydroxide was added drop by drop. The precipitate formed very rapidly until the liquid became alkaline. The liquid was filtered, and, because it gave no further precipitate with sodium hydroxide, acidified with hydrochloric acid, and the remaining rare earths thrown out as oxalates.

At. wt. of fraction.....	(1)101.75	(2)98.30
Grams.....	6.28	2.19

Fractional Precipitation by Means of Tartaric Acid from Acetone.—Ten grams of oxides were dissolved in nitric acid and evaporated to crystallization so as to remove the excess of nitric acid. The nitrates were then dissolved in acetone and diluted to 300 cc. Acetone saturated with tartaric acid, by shaking with the finely ground material, was added by means of a buret. Five fractions were obtained in this manner, the sixth being obtained by means of oxalic acid.

Acetone added (cc.)...	(1)13	(2)16	(3)17	(4)20	(5)45	(6) ..
At. wt. of fraction.....	100.15	99.7	101.15	100.65	101.10	101.8
Grams.....	0.45	0.65	0.98	0.90	1.71	4.71

This method which was published by O. J. Barnebey¹ appears not to be adapted for the separation of yttrium and erbium.

Fractional Precipitation by Means of Malonic Acid from Acetone Solution.—The acetone solution of the rare earth nitrates was prepared as described above. Four fractions were obtained by adding an acetone solution of malonic acid. The first two fractions were obtained by allowing the malonates to separate from the cold solution, while the last were precipitated from a boiling solution. A fifth fraction was taken by the use of oxalic acid.

At. wt. of fraction.....	(1)98.8	(2)99.4	(3)102.4	(4)102.5	(5)100.2
Grams.....	0.86	1.15	0.69	0.96	4.36

Conclusion.

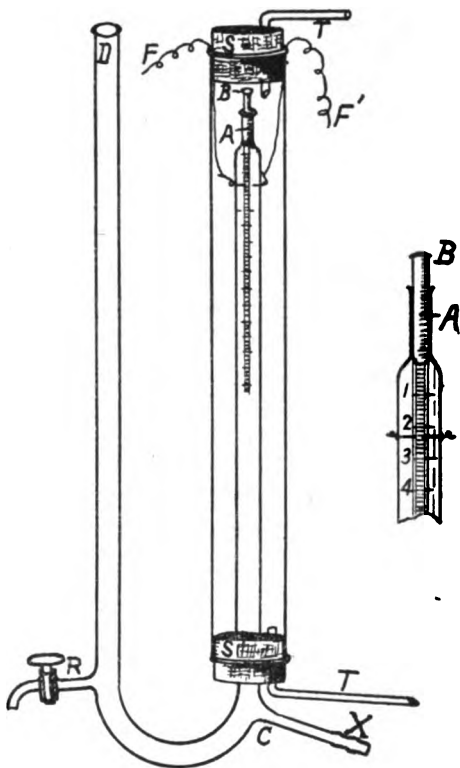
It is evident from the preceding results that three methods stand out as being best adapted for the separation of erbium from yttrium. These include the nitrite, cobalticyanide and phosphate processes. The sodium nitrite is probably the best for large scale work owing to its cheapness, and ease of manipulation.

DURHAM, N. H.

¹ THIS JOURNAL, 34, 1174 (1912).

NOTES.

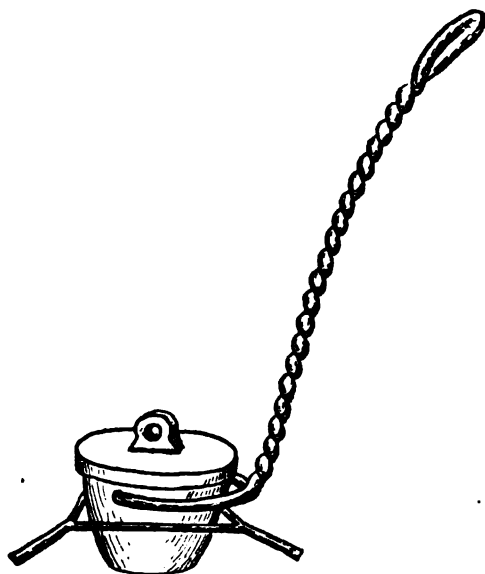
An Improvement of Hoffman's Eudiometer.—The stopcock of the Hoffman eudiometer, which is used to demonstrate the volumetric composition of water, is liable to break when it is heated with steam. We have found that it is an advantage to replace this stopcock with a ground glass stopper, A (see fig.), which is of conical shape, having the larger part below and provided with a glass flange, B, which prevents the stopper, when it is loosened, from falling through the top of the buret. In order to fill the eudiometer the stopper is pushed down, leaving the flange resting on the top of the tube. The electrolytic gas is then allowed to enter through the side tube X. As it rises it drives the air completely from the walls between the mercury and the glass. After a short time the eudiometer is closed by pulling the stopper up. The stopper should be lubricated slightly with lanoline or some other suitable lubricant. The outer tube is then adjusted and the whole heated in the current of steam and the remainder of the operation carried out as usual. In addition to the fact that the stopcock is less liable to break than the usual stopcock, it occupies less space in the larger tube through which the steam passes.



GAETANO MAGNANINI AND A. VENTURI.

MODENA, ITALY.

A Crucible "Fork."—This little device has been in use in the laboratories of William Jewell College for some time and has proved very practical and convenient. It was designed for the use of students in elementary classes but may appeal to chemists in general. The fork is made of stout aluminum wire. The prongs of the fork enclose slightly more than a semicircle and should be bent to fit the crucible used. The space be-



tween the ends of the prongs should be large enough to pass around the crucible when supported on a tripod, but small enough to prevent the crucible from slipping out when the fork is lifted. When properly adjusted the crucible is held very securely.

H. G. PARKER.

WILLIAM JEWELL COLLEGE,
LIBERTY, MISSOURI.

An Inexpensive Dialyser for Class Use.—The glass dialysing frames are too expensive for use by classes in colloids. Even the goldbeater's skin to be stretched

over these frames is not cheap. Such expense is a handicap on colloid research and discouraging.

If a very wide-mouthed bottle is at hand the bottom may be cracked off by a hot wire on a file mark, a membrane tied over the lip on the mouth of the bottle and a good dialyser of trifling cost is ready. This type is not new, of course, but deserves to be better known. If a large number of rather small dialysers are needed, test tubes may be adapted by cutting off the bottom in the same way or heating and blowing out the ends. The lip on the test tube permits secure attachment of the membrane with a rubber band.

The cheapest and most easily made dialyser I have used is a sheet of parchment paper shaped like a beaker. In other words it is all membrane having much greater dialysing surface than the usual forms. These beakers or cups can be shaped easily by any student. A sheet of parchment free from pinholes is soaked in water a few minutes to soften it and then folded over a bottle of the desired size and shape. The folds should be triangular, narrow and cover each other much as do the folds of an umbrella. It is best to crease them with firm pressure. A cord is tied around the paper and bottle about one centimeter from the upper edge and the whole set aside to dry. When dry the bottle is removed and the cup holds its shape perfectly. The cord must be left on the cup to support the sides. Two holes may be punched near the top of the paper and a string attached like the handle of a pail. So tough is the paper that a parchment cup holding a liter of water may be carried without tearing or

collapsing. Trimming the upper edges of the cup gives a neater appearance.

To use such a dialyser it is nearly filled with the colloidal solution and suspended in a large vessel of pure water. Removal of ions is extremely rapid in spite of the fact that parchment is inferior as a membrane to goldbeater's skin. It is evident that with a given membrane the rate of dialysis is proportional to the effective surface of the membrane. In this form the bottom and sides of the cup are all effective.

The rate of dialysis may be doubled if two such cups are used, the smaller inside the larger. The inner cup holds pure water and the other the colloidal solution, while the combination of cups is hung in a larger vessel of pure water. This arrangement gives dialysing surface outside and inside the colloidal solution. The water may be changed as desired. It is quite possible that this simple method of making parchment cups may have been used by others but I have found no reference to it in the literature.

HARRY N. HOLMES.

OSHERLIN COLLEGE,
OSHERLIN, OHIO.

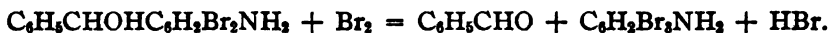
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

SOME REACTIONS RESULTING IN THE CLEAVAGE OF POLYNUCLEAR AROMATIC COMPOUNDS.

BY E. P. KOHLER AND R. H. PATCH.

Received March 20, 1915.

In 1911 Clarke and Esselen¹ found that when bromine reacts with *p*-aminobenzhydrol the principal result is not a brominated hydrol but a mixture of two mononuclear compounds: benzaldehyde and a substitution product of aniline. They then studied the action of bromine on a number of derivatives of *o*- and *p*-aminobenzhydrol and found that all of these behaved in a similar manner. A typical reaction is represented by the equation



All of the experiments of Clarke and Esselen were made with derivatives of diphenylcarbinol, but Clarke and Patch² subsequently extended the investigation to derivatives of triphenyl carbinol, and to amino alcohols that have aliphatic as well as aromatic groups. The results reported in this paper were obtained in continuation of that investigation.

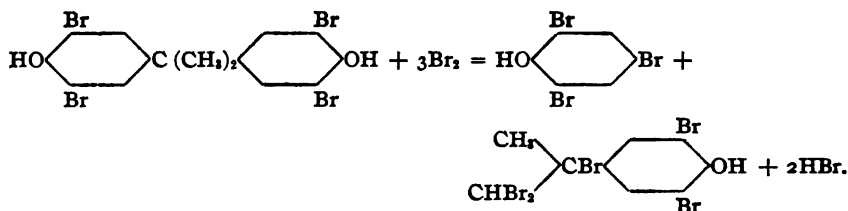
That halogens occasionally replace an aliphatic side chain in aromatic compounds, or split diphenylmethane derivatives into mononuclear compounds has long been known. As early as 1845 Piria³ found that

¹ THIS JOURNAL, 35, 1135 (1913); 36, 308 (1914).

² *Ibid.*, 34, 912 (1912).

³ *Ann.*, 56, 47 (1845).

chlorine transforms *o*-hydroxybenzyl alcohol into trichlorophenol and Visser,¹ later, obtained a corresponding result with bromine. Since then isolated instances of a similar result have been recorded by various observers; but the only systematic investigations of the subject were made by Zincke² and by Auwers³ in connection with their work on pseudo phenols. Zincke used alkylated diphenylmethane derivatives that had hydroxyl groups in the para position and found that bromine invariably splits these into mononuclear compounds. A typical case is illustrated by the equations



Auwers worked with *p*-dihydroxydiphenylmethane derivatives that had alkyl groups in the nucleus. He found that when these react with bromine the result is almost invariably a mixture of substitution and cleavage products. By comparing the behavior of five closely related substances he showed that the relative amount of cleavage depends upon the number and location of the alkyl groups in the diphenylmethane derivative.

Neither Zincke nor Auwers found a satisfactory explanation for this cleavage by bromine. Zincke inclined to the view that cleavage was due to the direct action of bromine upon the diphenylmethane derivative, and that the bromine substitution products were due to subsequent bromination of one of the cleavage products; but he also admitted that his facts could be interpreted equally well on the assumption that substitution in the alkyl groups was the primary process and that cleavage was due to the resulting hydrobromic acid. Auwers attributed cleavage to hydrobromic acid and, in support of this view, established the fact that no cleavage occurred when his substances were treated with bromine in the presence of enough potassium acetate to react with all of the hydrobromic acid formed by substitution. But Auwers could not explain the fact that no cleavage occurred when his substances were heated with hydrobromic acid instead of bromine.

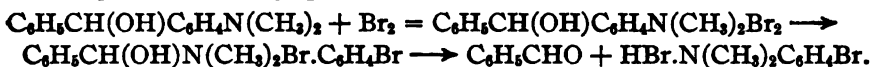
The most significant fact brought to light by Clarke and Esselen, is the astonishing ease with which the amino derivatives of diphenylcarbinol undergo cleavage into mononuclear compounds under the influence of bromine. Zincke usually heated his substances with excess of bromine

¹ *Arch. der Pharm.*, **235**, 591 (1897).

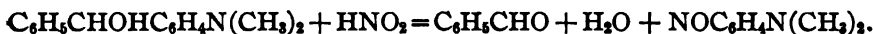
² *Ann.*, **343**, 76 (1905).

³ *Ibid.*, **356**, 175 (1907).

to 100° in sealed tubes. Auwers added bromine to boiling solutions of his compounds in glacial acetic acid. Clarke and Esselen found that the amino hydrols react rapidly at 0° in any indifferent solvent. In explanation, they attribute cleavage to a mechanism similar to that adopted by Hantzsch and Graf to account for the easy bromination of aromatic amines. They assume that bromine first combines with nitrogen to form a perbromide, and that this subsequently undergoes a series of rearrangements resulting in the cleavage products obtained.



The results recorded in this paper show that the rapid, easy cleavage of hydrols is not confined to the action of halogens. Nitric acid, nitrous acid, and other reagents that are capable of forming substitution products by direct action upon aromatic compounds, split the hydrols in the same manner and with the same ease as do the halogens, and the substances that give a large proportion of cleavage products when treated with halogens, undergo an equally extensive cleavage under the influence of these reagents. Dimethylaminobenzhydrol and nitrous acid, for example, react almost quantitatively in accordance with the equation



The results also show that cleavage is not confined to hydrols that contain the amino or substituted amino groups. Any group that effectively promotes substitution in the nucleus of aromatic compounds will similarly promote cleavage in the case of hydrols. These groups are not, however, equally effective, and we have tried to find a quantitative expression for the relative effectiveness of different groups.

The reactions that may take place when a substance like dimethylaminobenzhydrol is treated with bromine are as follows:

I. Replacement of one or more hydrogen atoms in the α -position to the amino group by bromine.

II. Cleavage, both of the original substance, and of the substitution product formed in I.

III. Formation of an ether from two molecules of the hydrol—a process that readily takes place in the presence of small quantities of hydrobromic acid.

IV. Oxidation of the hydrol to the corresponding ketone.

Of the products formed in these reactions, only those resulting from cleavage are readily volatile with steam. By distilling with steam, oxidizing the aldehyde, and extracting and weighing the benzoic acid, it was generally possible to make a sufficiently accurate estimate of the amount of cleavage. These determinations warrant the following general statements:

I. Whenever the reaction takes place rapidly, so that for each molecule of hydroxyl compound one molecule of bromine or other suitable reagent disappears as fast as it is added, the result is almost exclusively cleavage and substitution. The groups whose presence in the para position leads to this result may be regarded as the most effective groups. When the reagent disappears more slowly and less completely, both cleavage and substitution diminish in favor of oxidation and ether formation. With hydrols that have a methyl group or a halogen atom in the para position, there is barely enough cleavage or substitution to be detected.

The relative amounts of cleavage and substitution depend upon the character of the "bridge," under conditions under which a given benzhydrol derivative gives principally cleavage products, the corresponding diphenylmethane derivative undergoes but little cleavage, while the corresponding ketone will give only substitution products.

II. The efficiency of different groups in promoting cleavage is represented by the following series, in which the most effective comes first: $(\text{CH}_3)_2\text{N}$, HO, CH_3O , CH_3 , Br.

III. Substituents in the *o*-position to these groups invariably diminish the relative amount of cleavage and with all but the most effective, di-ortho substitution stops it altogether.

These facts show that cleavage and replacement of hydrogen are similar processes, promoted equally by the same groups, hindered in the same way, therefore the result of the same mechanism.

I. Experiments with Amino Compounds.

***p*-Dimethylaminobenzhydrol and Bromine.**—The reaction between these substances in chloroform has been described by Clarke and Esselen. For the purpose of determining the influence of the solvent we compared the results obtained in chloroform with those obtained in glacial acetic acid, and in dilute hydrochloric acid. We found that the products are the same in all cases, but that, possibly owing to salt formation, the reaction goes more slowly in the acid solvents. We also examined the behavior of the hydrol towards concentrated hydrobromic acid. For this purpose a solution of the hydrol in hydrobromic acid (sp. gr. 1.78) was allowed to stand in a glass stoppered bottle for 11 days, then diluted with water and neutralized. A faint odor of benzaldehyde was perceptible, but the usual procedure did not give enough benzoic acid even for a melting-point determination. Cleavage, therefore, is not due to hydrobromic acid.

***p*-Dimethylaminobenzhydrol and Nitrous Acid.**—A dilute aqueous solution of sodium nitrite was added, very gradually, to a solution of five grams of the hydrol in 12.5 cc. of concentrated hydrochloric acid and 25 cc. water, that was cooled to 0°. The nitrous acid disappeared as fast as formed and none could be detected in the solution with starch-iodide

paper until slightly more than one equivalent of sodium nitrite had been added. The solution at first turned orange, then deposited an orange-colored precipitate. This soon disappeared, however, and as more nitrite was added a yellow crystalline deposit took its place and oily drops of benzaldehyde collected on the surface of the liquid. As soon as free nitrous acid appeared in the solution, the precipitate was filtered off, washed with alcohol containing hydrochloric acid, dried, and weighed. The crude salt melted at 173–174°. As the melting point of pure nitrosodimethyl aniline hydrochloride is 177°, this was nearly pure salt and the 3.45 g. obtained show 94% of cleavage. The salt was decomposed with a solution of potassium carbonate, the base recrystallized and identified as nitrosodimethyl aniline—a brilliant green solid melting at 85–86°.

***p*-Dimethylaminobenzhydrol and Nitric Acid.**—The experiments with nitric acid were carried out in glacial acetic acid or, in specified cases, without use of solvent. The reaction was invariably accompanied by the evolution of oxides of nitrogen indicating oxidation by nitric acid. Experiments with benzhydrol showed that cold, concentrated nitric acid does not oxidize hydrols to benzoic acid. Any benzoic acid obtained in the reaction between substituted hydrols and nitric acid must therefore be due to the intermediate formation of benzaldehyde by cleavage. The oxidation of these hydrols with cold neutral permanganate also stops when the hydrol has been oxidized to the corresponding ketone. For these reasons it was not necessary to isolate the benzaldehyde first and then oxidize it to benzoic acid. A more accurate value for the amount of cleavage was obtained, in some cases, by diluting the reaction mixture with water, neutralizing with soda, oxidizing with permanganate in the cold, removing the oxides of manganese with sulfur dioxide, and finally extracting and weighing the resulting benzoic acid.

The reaction between *p*-dimethylaminobenzhydrol and nitric acid¹ was carried out with 5 g. of hydrol, dissolved in 30 g. of glacial acetic acid, and 20 g. of nitric acid (sp. gr. 1.50) added, the mixture being cooled with running water both while the acid was added and afterwards as long as heat was given off. Oxidation of the product, which had a strong odor of benzaldehyde, with permanganate gave 0.65 g. of benzoic acid—showing 28% cleavage. Owing to the ease with which the hydrols are oxidized to ketones by nitric acid, the proportion of cleavage products is smaller than with other reagents.

Ethyl Ether of *p*-Diethylaminobenzhydrol and Bromine.—According to the mechanism that Clarke and Esselen proposed to account for the splitting of carbinols, no cleavage would be expected in the case of ethers. The ether we used was made by the method of Willstätter.² A test

¹ See Zincke, *Ann.*, 362, 203 (1908); Pinnow, *Ber.*, 27, 3163 (1894).

² *Ber.*, 39, 3765 (1906).

with ethyl magnesium bromide showed that it was free from hydrol, but it rapidly decolorized bromine, and at least a third of it was split in the usual way. The products identified were benzaldehyde and *p*-bromodimethyl aniline. Special search was made for ethyl bromide, but neither this nor ethyl alcohol could be detected among the products, hence the fate of the ethyl group remains unknown. The results are inconclusive, because, as usual, some replacement of hydrogen by bromine occurred and therefore some hydrobromic acid was formed. Although every precaution was taken to avoid the presence of water, it is possible that the hydrobromic acid transformed some of the ether into diethyl-aminobenzhydrol, and that this was responsible for the cleavage products.

Ethyl-di-(4-dimethylaminophenyl) Carbinol, $(C_2H_5)((CH_3)_2NC_6H_4)_2COH$, was prepared by the action of ethylmagnesium bromide on Michler's ketone. As the ketone is sparingly soluble in ether, and too vigorous reaction readily leads to the formation of an ether in place of the carbinol, the procedure adopted was as follows: A solution of the ketone in pure, dry benzene was dropped, slowly, into an ethereal solution that contained an excess of ethyl magnesium bromide, and was cooled in a freezing mixture. Each drop of the ketone solution produced an orange-colored precipitate that redissolved on shaking. The mixture was allowed to stand at the ordinary temperature for 36 hours, then poured into excess of iced sulfuric acid. A part of the product remained in the ether-benzene layer which deposited it in crystalline form on evaporation. The remainder dissolved in the acid, from which it was recovered by neutralization with ammonia in the presence of ammonium chloride. The carbinol was purified by recrystallization from a mixture of benzene and ligroin. The yield was 92 g. from 100 g. of ketone—82% of the calculated quantity.

Calc. for $C_{19}H_{28}ON_2$: C, 76.51%; H, 8.72%. Found: C, 76.02%; H, 8.37%.

The substance is sparingly soluble in ligroin and cold ether, readily in boiling ether and other common organic solvents. It melts at 118° .

Reaction with Bromine.—A solution of 8 g. of bromine in chloroform was added to a solution of 14.9 g. of the carbinol in the same solvent. Reaction took place immediately but there was no evidence of an intermediate addition product. The residue left after evaporating the chloroform in a current of air was made alkaline with sodium hydroxide and distilled with steam. The distillate contained 6.7 g. of *p*-bromodimethyl aniline, melting at 54° , showing that cleavage in this case amounted to at least 67%. All attempts to get the second product of the reaction in pure condition, or in the form of some crystalline derivative failed.

Naphthyl-(4-dimethylaminophenyl) Carbinol and Bromine.—Pure carbinol, prepared by the method of Sachs,¹ was dissolved in chloroform and this solution treated with a slight excess of bromine in the same solvent.

¹ *Ber.*, 38, 516 (1905).

Here also we could secure no evidence that an intermediate addition product was formed at low temperatures. After the solution had stood at the ordinary temperature for a few minutes, the excess of bromine and the solvent were removed in the usual way. The residue was poured into water containing enough acid to combine with any amine present and distilled with steam. The distillate, which held a yellow oil in suspension, was extracted with chloroform. The resulting chloroform solution, when diluted with alcohol and digested with a solution of *o*-nitrophenylhydrazine in dilute acetic acid, deposits a hydrazone in bright red needles melting at 179–180°. The analysis showed that this was the nitrophenylhydrazone of naphthoic aldehyde.

Calc. for $C_{17}H_{12}O_2N_2$: N, 14.4%. Found: N, 14.8%.

The residue left in the distilling flask was made strongly alkaline and again distilled with steam. The crystals that separated from the distillate were *p*-bromodimethyl aniline, melting at 54°. As the object of this experiment was the detection of any intermediate compound that might be formed, the relative amount of cleavage products was not determined.

Methylphenyl-(3-bromo-4-dimethylaminophenyl) Carbinol, $(CH_3)_2(C_6H_5)[C_6H_3(Br)N(CH_3)_2]COH$ was made by adding 30 g. of finely powdered bromodimethylaminobenzophenone to a cooled solution obtained by dissolving 4.7 g. magnesium in an ethereal solution of 30 g. of methyl iodide. The mixture was allowed to stand overnight at the ordinary temperature, then poured into a separatory funnel containing cracked ice, ammonia, and ammonium chloride. The ethereal layer, after drying over anhydrous potassium carbonate and evaporation, left an oil. As this could not be induced to crystallize it was transformed into the oxalate by shaking the ethereal solution with a concentrated aqueous solution of oxalic acid. The oxalate separated in colorless crystals that were washed with water and ether. A bromine determination showed that these were pure oxalate.

Calc. for $C_{18}H_{20}O_4NBr$: Br, 19.51%. Found: Br, 19.45%.

The free base was liberated by shaking the pure oxalate with excess of potassium hydroxide, but the product purified in this way likewise was an oil that would not crystallize. Owing to the ease with which it loses water, it could not be distilled under diminished pressure. It was therefore dried and used without further attempt at purification.

Reaction with Bromine.—The reaction was carried out at -10° with 5 g. of carbinol dissolved in chloroform, the bromine being added until it was plainly in excess. The product was poured into dilute sulfuric acid and distilled with steam. The distillate contained 1 g. acetophenone, showing that 53% of the carbinol had undergone cleavage, as compared with 70% obtained in the case of the corresponding bromine-free compound.

Methylphenyl-(3-bromo-4-dimethylaminophenyl) Carbinol and Nitrous Acid.—The behavior of this substance is in sharp contrast with that of dimethylaminobenzhydrol. When a solution of sodium nitrite was added to a solution of the hydrol in hydrochloric acid, free nitrous acid appeared in the solution before a third of one equivalent had been introduced and no acetophenone or other cleavage product could be detected. The bromine in the *o*-position to the dimethylamino group evidently stops cleavage by nitrous acid as effectively as substituents in this position stop the introduction of a nitroso group in the *p*-position of amines.¹

II. Experiments with Hydroxyl and Methoxyl Compounds.

***p*-Hydroxybenzhydrol and Bromine.**—As the hydrol is sparingly soluble in chloroform the reaction in this case was carried out in glacial acetic acid. It took nearly 6 atoms of bromine to produce a permanent color and about 3 hours to complete the reaction. The acid was then neutralized with soda and the resulting liquid distilled with steam. The distillate contained benzaldehyde, which was removed with bisulfite, and tribromophenol, which was identified by making a mixed melting-point determination with a sample on hand. The residue left after the steam distillation was crystallized from benzene. It separated in white needles that melted, with decomposition at 164°.

Calc. for $C_{12}H_{10}O_2Br_3$: Br, 44.69%. Found: Br, 44.5%.

This substance was identified as 3,5-dibromo-4-hydroxybenzhydrol, which had previously been obtained by Zincke from 3,5-dibromo-4-hydroxydiphenylmethane.²

All of the products were isolated in this case, and by weighing these it was possible to determine the relative amounts of cleavage and substitution with considerable accuracy. We found that the result depends to some extent upon the rate with which the bromine is added; when it was added very slowly the cleavage products represent 33% of the hydrol used. This was increased to 42% when all of the bromine was added at once.

Anisalccohol and Bromine.—Anisalccohol dissolved in chloroform readily reacts with bromine. There is some replacement of hydrogen by bromine, but even at -15° a considerable part of the alcohol undergoes cleavage into *p*-bromoanisol, formaldehyde, and hydrobromic acid. The hydrobromic acid transforms some of the alcohol into *p*-methoxybenzylbromide and water which accumulates on top of the chloroform solution. By allowing the reaction to proceed in the presence of excess of finely divided mercuric oxide it was possible to remove the hydrobromic acid as fast as formed. This prevented the formation of methoxybenzylbromide,

¹ *Monatsh. Chem.*, 19, 627 (1898).

² *Ann.*, 334, 367 (1904).

but the cleavage into bromanisol and formaldehyde took place as before. Cleavage is therefore not due to hydrobromic acid but to bromine.

***p*-Methoxybenzhydrol**, $(\text{CH}_3\text{OC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CHOH}$.—The alcohol was obtained by Busch¹ when he added sodium nitrite to the hydrochloride of methoxybenzhydramine. As anisic aldehyde can be obtained in quantity we undertook to make it by treating the aldehyde with phenyl magnesium bromide in the usual way. Twenty-seven grams of aldehyde gave 20 g. of a mixture of solid products. By repeated recrystallization from ligroin the mixture was separated into the desired alcohol and a less soluble substance that crystallized in colorless needles melting at 120°. This proved to be *p*-methoxybenzhydrol ether.

Calc. for $\text{C}_{13}\text{H}_{12}\text{O}_2$: C, 81.95%; H, 6.34%. Found: C, 82.2%; H, 6.2%.

As the Grignard reaction always gave a mixture, we subsequently tried the reduction of methoxybenzophenone with sodium amalgam and found this the most satisfactory method of preparation. Excess of sodium amalgam was added to a solution of the ketone in alcohol, the mixture allowed to stand overnight, then boiled for six or seven hours and finally poured into a large quantity of water and allowed to stand until the oil had solidified. The solid was recrystallized from ligroin. It separated in large transparent needles that melted at 60° (Busch 58°).

***p*-Methoxybenzhydrol and Bromine**.—The reaction was carried out in chloroform. As the bromine was added, the solution assumed a pink color similar to that of the solid addition product which is obtained when bromine is added to anisic aldehyde. The color soon disappeared, however, hydrobromic acid appeared and a liquid collected in the solution. Benzaldehyde and *p*-bromoanisol were obtained as cleavage products, and the usual method of procedure showed about 20% of the possible amount of cleavage.

***p*-Methoxybenzhydrol and Nitric Acid**.—About 7.5 g. of nitric acid were added gradually to a cooled solution of 4 g. of the hydrol in 10 cc. of glacial acetic acid and the mixture allowed to stand for several days. In this case the product was poured into water and the volatile constituents separated by distillation with steam. The distillate contained benzaldehyde, which was oxidized to benzoic acid and extracted with soda, and *p*-nitroanisol which was identified by comparison with a sample on hand. The pasty residue left in the distilling flask was extracted with naphtha. This dissolved most of it, leaving a small quantity of a colorless solid. The naphtha on evaporation deposited faintly red crystals melting at 55–6°, identified as slightly impure hydrol. The solid, insoluble in naphtha was recrystallized from 80% alcohol, which deposited it in pale yellow needles melting at 104°. The analyses show that this is nitromethoxybenzhydrol, $(\text{CH}_3\text{O})(\text{NO}_2)\text{C}_6\text{H}_3\text{CHOHC}_6\text{H}_5$.

¹ *J. prakt. Chem.*, [2] 77, 20 (1905).

Calc. for $C_{14}H_{13}O_4N$: C, 64.9%; H, 5.0%. Found: C, 64.8%; H, 4.4%; C, 64.6%; H, 4.6%.

In this case all of the hydrol could be accounted for; the sole products of the reaction were: a nitro derivative of the hydrol formed by substitution, and benzaldehyde and *p*-nitroanisol resulting from cleavage. As a part of the hydrol did not participate in the reaction it is not possible to calculate the extent of cleavage with accuracy, but the amount of benzoic acid obtained showed that it must have been considerable. Somewhat different results were obtained when the hydrol was added directly to the carefully cooled nitric acid. The substances formed were the same as those obtained in the presence of acetic acid, but the principal product was the nitro hydrol resulting from substitution.

The Ethyl Ether of Methoxybenzhydrol, $C_6H_5(CH_3OC_6H_4)CHOC_2H_5$, was made by treating anisic aldehyde with phenyl magnesium bromide as described in the preparation of methoxybenzhydrol. The mixture was boiled for an hour, then cooled in a freezing mixture and treated with acetyl chloride that had been freed from hydrochloric acid by distillation with diethylaniline. A vigorous reaction took place and was completed by warming on a steam bath for half an hour. The mass was then poured into iced acid, and the solution distilled with steam for a short time to remove solvent, bromobenzene and diphenyl. This left a gummy solid—presumably of acetyl compound—which was boiled with alcohol for three or four hours, and finally distilled under diminished pressure. Most of the product distilled at 258–260° under a pressure of 25 mm.

Calc. for $C_{18}H_{19}O_3$: C, 79.3%; H, 7.4%. Found: C, 78.9%; H, 7.4%.

The ether was obtained as a pale yellow oil that did not solidify at -17° .

Reaction with Bromine.—This ether, like that of dimethylaminobenzhydrol, reacted with bromine as readily as the hydrols. The product was first distilled from a water bath to remove the chloroform used as solvent and then under diminished pressure to separate the cleavage products from those due to substitution. The chloroform gave iodoform when shaken with iodine and potassium hydroxide, showing the presence either of alcohol or ethyl bromide, probably the latter because the chloroform that was used was free from alcohol and precautions were taken to avoid the presence of water. The vacuum distillation gave benzaldehyde and *p*-bromoanisol as cleavage products. The amount of cleavage, calculated from the weight of *p*-bromoanisol obtained, was slightly under 10%.

The Ethyl Ether of *p*-Methoxybenzhydrol and Nitric Acid.—The reaction was carried out like that with the hydrol itself and it gave the same products. About 10% of the substance appeared in the form of cleavage products; but as the substitution product that was obtained was the nitro hydrol, it is evident that the ether was decomposed at some

stage in the process and it was not possible to determine whether this preceded or followed cleavage.

3-Bromo-4-methoxybenzhydrol, $C_6H_5[C_6H_4(Br)(OCH_3)]CHOH$, was made by adding bromo anisic aldehyde to phenylmagnesium bromide in ethereal solution and allowing the mixture to stand in the cold. The resulting magnesium compound was decomposed with iced ammonium chloride, the volatile substances removed by distillation with steam and the residue recrystallized from naphtha or 50% alcohol. It is readily soluble in all organic solvents except petroleum ether and naphtha, and melts at 79° .

Calc. for $C_{12}H_{11}O_2Br$: Br, 27.3%. Found: Br, 27.2%.

The reaction with bromine was carried out at the ordinary temperature and the amount of benzaldehyde that was formed was determined in the usual way. This showed only about 7.5% of cleavage. The bromine in the *o*-position to the methoxyl group therefore greatly reduces, but does not entirely prevent, cleavage.

3,5-Dibromo-4-hydroxybenzhydrol was also treated both with bromine and with concentrated nitric acid but we could get no evidence of cleavage with either reagent.

Phenyltolylcarbinol and Bromine.—Thirty grams of bromine were added to a solution of 60 g. of the carbinol in 150 cc. of chloroform. The reaction started immediately, heat was given off and a heavy liquid began to accumulate below the chloroform. The reaction soon became slower and, although less than one equivalent of bromine had been added, some remained after the mixture had stood for three days, but this rapidly disappeared when the solution was exposed to sunlight. The lower layer was found to be a saturated solution of hydrobromic acid in water. After this had been removed enough additional bromine was added to bring the total amount to one equivalent. This was decolorized very rapidly on exposure to sunlight, but no more water was formed. The mixture was then distilled with steam. The first portions of distillate had the odor of benzaldehyde, indicating some cleavage, but the amount was extremely small. The latter distillates contained a colorless oil that solidified on standing. The solid was found to be unchanged carbinol. From the nonvolatile residue ether extracted a solid that after recrystallization melted at 105° . The analyses show that this was phenyltolyl carbiny ether.

Calc. for $C_{20}H_{18}O$: C, 88.9%; H, 6.9%. Found: C, 88.7%; H, 7.0%.

The remainder of the product was an oily mixture of halogen compounds that decomposed when distilled under diminished pressure. These results indicate that when the group in the para position is no more effective than an alkyl group, bromine, in the cold, and in the dark, oxi-

dizes a part of the hydrol to the ketone and transforms the rest into the ether.

CAMBRIDGE, MASS.

CRYSTALLINE β -METHYL FRUCTOSIDE AND ITS TETRACETATE.¹

BY C. S. HUDSON AND D. H. BRAUNS.

Received March 20, 1916.

In a previous article² several methods for the preparation of tetracetyl fructose were described and it was shown that the action on fructose of acetic anhydride containing ZnCl_2 gives the best result and yields about 36% of the theory. This easily prepared crystalline tetracetate is a convenient material from which to start the preparation of various fructose derivatives and in the article mentioned its conversion to α -pent-acetyl fructose was described. We have now sought to use it in the preparation of a monomethoxy derivative of fructose, and have applied to it the method of methylation with methyl iodide and silver oxide which was devised by Purdie.³ Although this method has been applied with good success to the preparation of methylated derivatives of many of the sugars, particularly by Irvine and his co-workers, fructose has never yielded but two pure derivatives. Purdie and Paul⁴ prepared tetramethyl fructose in crystalline form, and Irvine and Hynd⁵ obtained a crystalline monomethyl fructose by the methylation of fructose diacetone and showed that the methoxy group in it is attached to the terminal carbon atom farthest from the ketonic carbon. Our results show that Purdie's method of methylation succeeds excellently with fructose tetracetate and gives almost a quantitative yield of pure crystalline tetracetyl monomethoxy fructose, the acetyl groups of the tetracetate not being affected by the methyl iodide of neutral reaction. The substance crystallizes very well from petroleum ether in long prismatic needles. Its saponification with barium hydroxide has yielded a crystalline monomethoxy fructose which does not reduce Fehling's solution until after hydrolysis by acid. This reaction differentiates the substance from Irvine and Hynd's monomethoxy fructose, which reduces strongly, and proves that our crystalline material is *methyl d-fructoside*. On the probable assumption that it is a γ -cyclo derivative, its constitution is

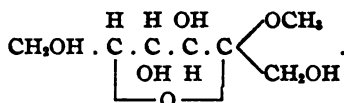
¹ Contribution from the Carbohydrate Laboratory, Bureau of Chemistry, United States Department of Agriculture.

² THIS JOURNAL, 37, 2736 (1915).

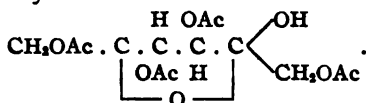
³ "A General Review of Purdie's Reaction," by Charles Robert Young, Memorial Volume of Scientific Papers of St. Andrews University, 500th Anniversary.

⁴ J. Chem. Soc., 91, 289 (1907).

⁵ Ibid., 95, 1220 (1909).

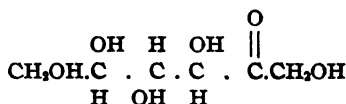


Its formation from *tetracetyl d-fructose* establishes the configuration of that substance similarly as



The high negative rotation of methyl fructoside (-172 in water) in comparison with that of β -fructose (-133 in water) indicates that it is a beta derivative. It is not hydrolyzed by the enzymes of yeast nor by emulsin and does not show mutarotation, behaving quite like the only other known methyl ketoside, methyl *l*-sorbose.¹

¹ Fischer, *Ber.*, 28, 1145 (1895). The antipode has been prepared by Lobry de Bruyn and van Ekenstein (*Rec. trav. chim.*, 19, 1 (1900)). There appears to be sufficient evidence at hand to permit the designation of this sorboside and its antipode as alpha derivatives, and, this being the case, their formation by the methylation of sorbose or its antipode with methyl alcohol and HCl falls in with what appears to be a general rule among the sugars that *this reaction produces the alpha isomer in considerable excess over the beta form*, doubtless because the equilibrium between the two isomers in methyl alcoholic solution is considerably towards the alpha form. The evidence in point consists in the fact that the specific rotation of methyl sorboside is -88 in comparison with -42 for sorbose. Since the structure of sorbose has been shown by Fischer to be



we consider that in the designation of the alpha and beta forms of its derivatives, according to the plan which one of us has suggested for the sugars (Hudson, *THIS JOURNAL*, 31, 72 (1909)), sorbose should be considered as a relative of *l*-glucose, because both may

OH
H

be regarded as higher sugars from *l*-glycerose, $\text{CH}_2\text{OH}.\text{C}.\text{COH}$. The designation of

H

the alpha and beta derivatives of *l*-glucose has been so made that the alpha form is more levorotatory than the beta, just as the alpha and beta forms of *d*-glucose have been so chosen that the alpha is more dextrorotatory than the beta. By this method of naming, α ,*l*-glucose is the optical antipode of α ,*d*-glucose, and β ,*l*-glucose and β ,*d*-glucose are likewise so related, which seems desirable in any system of nomenclature. Since sorbose is here considered as a levo sugar the possible alpha and beta *l*-sorbosides should be named so that the alpha form is the more levorotatory. Although only one methyl *l*-sorboside has been prepared in crystalline form, the fact that it is more levorotatory (-88) than the parent sugar *l*-sorbose (-42) indicates, by analogy with the other sugars, that the unknown *l*-methyl sorboside is less levorotatory than the sugar, and hence less so than the known *l*-sorboside; the latter is accordingly to be named the alpha form.

In this connection we would mention that sorbose has been designated by Fischer

Since the employment of tetracetyl fructose for the synthesis of other compounds makes knowledge of its structure desirable we thought it as *d*-sorbitose because on reduction it yields the same sorbite as does *d*-glucose. This designation was a subject of discussion between Rosanoff (THIS JOURNAL, 28, 114 (1906)), who suggested the name *l*-sorbitose on account of the structural relationship of the sugar to *l*-glycerose and *l*-glucose, and Fischer (*Ber.*, 40, 102 (1907)), who preferred *d*-sorbitose, because as a matter of history the structure of sorbitose was proved in part through the reduction of it and of *d*-glucose to the same form of sorbite. According to our understanding of Fischer's point of view, as given in his article, he regarded the naming as a matter of convention and preference, since the fundamental structure configurations which he proved for the sugars are in no way affected by the nomenclature that may be adopted for distinguishing the *d*- and *l*-forms of the sugars, and he was of the opinion that any advantage to be gained by changing his designation of sorbitose from *d*- to *l*- was not sufficient to outweigh the temporary confusion that always occurs when historical names are changed. Against this view it is to be said that at the present time the conditions are somewhat different from what they were in 1907 when the discussion between Rosanoff and Fischer took place, because it was not known at that time that a general relation exists in the sugar group between the rotatory powers of the alpha and beta forms of the sugars and their derivatives. The naming of these forms as alpha or beta according to this general relation among their rotatory powers, which seems very desirable because it furnishes in many cases at present the only method of distinguishing the members of the two series, becomes greatly confused unless the *d*- and *l*-forms of the sugars are selected on the basis of the structural relationships that follow from the cyanhydrin synthesis in the sugar group. We consider therefore that it is advisable, in order to prevent the increase of confusion in the nomenclature of the sugar derivatives, to apply the term *l*-sorbitose to the sugar which Fischer has shown to have the configuration mentioned. The other sugars to which the same remarks apply are xylose, gulose, idose and threose.

Irvine and Garrett (*J. Chem. Soc.*, 97, 1277 (1910)) have mentioned in connection with the provisional naming of the two fructose diacetones by Fischer (α -form, $[\alpha]_D^{20} = -161$ and β -form, $[\alpha]_D^{20} = -34$) that "the analogy to α - and β -glucosides in describing these compounds is not maintained in some respects. Thus the α -form * * * * is more easily hydrolyzed than the β -isomeride * * * *. This holds true not only for the removal of the acetone residue from the 3:4 position but also for the glucosidic acetone group." According to the plan which we are following the more levorotatory of these fructose diacetones should be designated the beta form and the other the alpha because fructose is a *d*-series sugar, and since Fischer's use of the α - and β -designations for these substances was only provisional, for the purpose of distinguishing them, we suggest that these names be now reversed, as indicated, since it is possible to assign the substances to the alpha and beta series on the basis of their rotations. When this is done it is seen that the analogy to α - and β -glucosides in regard to the relative ease of hydrolysis, holds. This may serve very well as an example of the advantages that come from a uniform system of naming the alpha and beta, and also the *d*- and *l*-, forms of the sugars, as it is probable that many more analogies between structure and physical properties or chemical reactivities will be found among the alpha and beta derivatives of the sugars.

Since Purdie and Paul's crystalline tetramethyl fructose shows mutarotation in water from $[\alpha]_D^{20} = -125$ to -121 , and Irvine and Hynd's monomethoxy fructose mutarotates from -70 to -53 , they are both to be regarded as beta derivatives. Likewise, Irvine and Garrett's fructose monacetone, $[\alpha]_D^{20} = -159$, is doubtless a beta compound because it was prepared from β -fructose diacetone, $[\alpha]_D^{20} = -161$.

well to regenerate crystalline fructose from it by saponification and definitely identify the sugar, which had not been done before.

It appears very probable on theoretical grounds that β -methyl fructose is one of the components of the uncrystallizable sirup which Fischer¹ obtained by the condensation of fructose with methyl alcohol, using HCl as a catalyst.

Experimental.

Preparation and Properties of β -Tetracetyl Methyl Fructoside.—Sixty grams of powdered fructose tetracetate, 375 g. of freshly prepared silver oxide and 340 cc. of methyl iodide were boiled on the water bath for six hours in a 2-liter Erlenmeyer flask with reflux condenser which was supplied with ice water in order to prevent loss of the solvent. The boiling of the methyl iodide (b. p. 44°) is not really essential because the reaction can be carried out quite as well at room temperature by shaking the mixture. In recovering the excess of MeI it is advisable to distil from a flask with a large bottom to prevent bumping. The residue from the distillation was mixed with some ether, filtered on a large Büchner funnel and the silver oxide washed with ether. The ether was evaporated in the air and the resulting colorless syrup soon crystallized. The first time that the reaction was carried out long standing of the sirup in a desiccator and occasional stirring with petroleum ether was necessary to induce crystallization, but in subsequent preparations crystallization took place readily even without seeding. The yield of the product, which was nearly pure as prepared, was almost the theoretical. For purification the crystals were boiled in a large flask with petroleum ether and the hot solution filtered and allowed to evaporate slowly in the air. In this way beautiful prismatic needles were obtained. The solubility of tetracetyl methyl fructoside in hot petroleum ether is only about 1 g. in 400 cc., but no other suitable solvent for recrystallization was found, as the substance is very soluble in all usual solvents excepting petroleum ether and water and in the latter it is almost insoluble. A second recrystallization from petroleum ether did not change the rotatory power or melting point. The substance melts at $75\text{--}76^\circ$, is colorless and odorless, and has a bitter taste. Analysis proves it to be a tetracetyl monomethoxy fructose.

0.2731 and 0.3082 g. substance gave 0.4982 and 0.5613 g. CO_2 and 0.1498 and 0.1682 g. H_2O .

Found: C, 49.75 and 49.67%; H, 6.14 and 6.10%. Theoretical for $\text{C}_6\text{H}_7\text{O}_7\text{OCH}_3(\text{C}_2\text{H}_3\text{O}_2)_4$: 49.70 and 6.12%.

A methoxyl determination with 0.2484 g. substance gave 0.1581 g. AgI corresponding to 8.41% OCH_3 . Theoretical 8.56%.

For the quantitative estimation of acetyl the substance was saponified by shaking 0.3000 g. with 75 cc. 0.1 *N* sodium hydroxide during one

¹ *Ber.*, 28, 1145 (1895).

hour at 0° and titrating with $0.1\ N$ sulfuric acid and phenolphthalein. The amount of acetic acid produced was found to be 66.45%. In a similar experiment of 2 hours' duration the value 66.31% was found and in a third lasting $2\frac{1}{2}$ hours the value was 66.19%. The theoretical quantity for a tetracetylmethyl fructoside is 66.30%. Evidently the saponification is complete after one hour.

The molecular weight was determined by the lowering of the freezing point of benzene. In three experiments, 1.4330, 3.1622 and 4.8405 g. β -tetracetyl methyl fructoside per 100 g. benzene gave the respective depressions 0.210° , 0.449° and 0.672° , from which the values 341, 352 and 360 are calculated for the molecular weight in comparison with the theoretical value 362.

The specific rotation was measured in chloroform solution. 2.000 g. of once recrystallized β -tetracetyl methyl fructoside were made up to 25 cc. with chloroform¹ and the solution was found to read in a 1 dcm. tube at 20° with sodium light 9.95 circular degrees to the left, hence $[\alpha]_D^{20} = -124.4$. After a second recrystallization from petroleum ether, the substance rotated 9.97 circular degrees to the left in a similar solution, hence $[\alpha]_D^{20} = -124.6$, which is taken as the specific rotation of pure β -tetracetyl methyl fructoside.

Preparation and Properties of β -Methyl Fructoside.—The method of saponification which was used for the quantitative estimation of acetic acid in β -tetracetyl methyl fructoside was found unsuitable for the preparation and isolation of β -methyl fructoside because the latter could not be obtained free from sodium acetate by repeated recrystallization from alcohol. The following procedure gave the desired result:

Seventy grams of crystalline barium hydroxide ($\text{Ba}(\text{OH})_2 + 8\text{H}_2\text{O}$) were dissolved in one liter of water on the steam bath and filtered into a bottle with a glass stopper. The solution was cooled with ice to about 5° , and although it was supersaturated at this temperature several experiments were performed without crystallization occurring. To it were added 20 grams powdered tetracetyl methyl fructoside, which required about half an hour's time, with occasional shaking, for complete solution. The liquid was kept one hour longer in ice and was then saturated with CO_2 and filtered. The amount of sulfuric acid necessary to precipitate the dissolved barium acetate was calculated to be 221.0 cc. normal H_2SO_4 , since this amount is equivalent to the acetic acid that is obtainable from 20 g. of tetracetyl methyl fructoside. A somewhat smaller amount, 210 cc. of acid, was added with stirring and the mixture was centrifuged for a couple of hours or kept in the ice-box for a couple of days in order to separate as much as possible of the suspended barium sulfate. The milky liquid

¹ *Chloroformum purificatum*, U. S. P.

was distilled *in vacuo* and some attention was needed in the beginning to prevent its foaming over into the receiver. After considerable concentration the solution could be filtered clear and by carefully adding 0.1 *N* H_2SO_4 to the filtrate it was brought to the stage where it gave only a slight precipitate with sulfuric acid. On evaporating this solution in a vacuum desiccator it soon crystallized to a solid mass. By repeated crystallization from hot absolute alcohol beautiful crystals were obtained which were free of ash. By slow evaporation large, thin plates were formed, which often measured 1 cm. square. The yield was about 80% of the theory.

β -Methyl fructoside melts at 119–120°. The crystals are colorless, odorless and have a pure, sweet taste. The taste of the α - and β -methyl glucoside is sweet followed by bitter. The fructoside is easily soluble in water and hot alcohol, slightly soluble in hot acetone and ethyl acetate. Its aqueous solution is not reduced by boiling with Fehling's solution. After hydrolyzing it by boiling its aqueous solution with a mineral acid and neutralizing the cooled solution, it readily reduces Fehling's solution on boiling. This reaction proves, in connection with the analysis recorded below, that the prepared substance is a methyl fructoside and also shows that in the described tetracetyl fructose the glucosidic hydroxyl is not acetylated.

0.2943 and 0.2246 g. subs. gave 0.4675 and 0.3576 g. CO_2 and 0.1905 and 0.1457 g. H_2O .

Found: C, 43.32 and 43.42%; H, 7.24 and 7.26%. Theoretical for $\text{C}_6\text{H}_{11}\text{O}_5(\text{OCH}_3)$: 43.27 and 7.27%.

A methoxyl determination with 0.2486 g. substance gave 0.2993 AgI corresponding to 15.92% OCH_3 . Theoretical 15.98%.

The molecular weight of the substance was determined by the lowering of the freezing point of water. In three experiments 1.2063, 2.5524 and 3.7749 g. in 100 g. water gave the respective depressions 0.13°, 0.259° and 0.384°, from which the values 172, 182 and 182 are calculated for the molecular weight in comparison with the theoretical value 194 for a methyl fructoside.

The specific rotation of the substance was measured in water. 2.5012 g. β -methyl fructoside were made up to 25 cc. with water and a reading of 17.2 circular degrees to the left was obtained in a 1 dcm. tube at 20° with sodium light; hence $[\alpha]_D^{20} = -171.9^\circ$. After a further crystallization from hot alcohol 2.5048 g. substance made up in the same manner rotated 17.23 circular degrees to the left; hence $[\alpha]_D^{20} = -172.1^\circ$, which is taken as the specific rotation of pure β -methyl fructoside.

In a high vacuum β -methyl fructoside can be sublimed. The sublimate was found to have the same melting point and specific rotation as men-

tioned above for the pure material prepared by crystallization from solvents.

The substance is not hydrolyzed by the enzymes of yeast or by emulsin. 0.100 g. β -methyl fructoside was dissolved in 10 cc. of water and after the addition of some fresh top fermentation yeast the solution was kept at room temperature in a fermentation tube. No gas was produced after 48 hours, but under the same conditions several cc. of CO_2 were produced from 0.100 g. fructose. For testing the action of emulsin a solution of 0.100 g. β -methyl fructoside in 8 cc. of water was mixed with 0.100 g. emulsin and the whole kept in a closed bottle at 35° for 48 hours, and as checks there were kept under the same conditions a solution of 0.100 g. amygdalin and 0.100 g. emulsin in 8 cc. of water and a mixture of 0.100 g. emulsin with 8 cc. water. After 48 hours the solutions were filtered and the filters washed with water. The three filtrates were boiled with Fehling's solution under the conditions of the quantitative determination of glucose by Allihn's method. Only the filtrate from the amygdalin mixture reduced Fehling's solution; the Cu obtained by glowing and reducing the precipitate weighed 0.1383 g. corresponding to 0.0703 g. glucose; calculated for 0.100 g. amygdalin, 0.0704 g. glucose.

Preparation of Crystalline Fructose from Fructose Tetracetate.—One hundred and forty grams of crystalline barium hydroxide ($\text{Ba}(\text{OH})_2 + 8\text{H}_2\text{O}$) were dissolved in two liters of water on the steam bath and filtered into a bottle with a glass stopper. The solution was cooled with ice to about 5° and 40 g. powdered tetracetyl fructose were added and the mixture occasionally shaken. After half an hour the crystals had dissolved. The solution was kept one hour longer in ice, then saturated with CO_2 and filtered. The amount of sulfuric acid necessary to precipitate the remaining barium acetate was calculated to be 459.7 cc. of $N \text{ H}_2\text{SO}_4$ and a somewhat larger amount, 463 cc. was added, with stirring, to the solution which was heated on the steam bath to about 50° . The barium sulfate was allowed to settle, the supernatant clear solution poured off and the remainder filtered. Barium hydroxide solution was carefully added to neutralize the excess of sulfuric acid and the filtered solution was evaporated *in vacuo* to a small volume. The clear solution, which contained only traces of barium acetate, was evaporated in a vacuum desiccator over potassium hydroxide to a thick sirup. The sirup was dissolved in warm absolute alcohol and the solution crystallized on standing in a desiccator. The crystalline fructose was separated by suction, taken up in a small amount of water and the solution filtered. After evaporation to a thick sirup the process for separating crystalline fructose was repeated and in this way 10.2 g. of pure crystalline fructose or 50% of the theory were obtained. The fructose melted at $102\text{--}104^\circ$, and its constant specific levorotation at 20° in an aqueous solution con-

taining 6.93 g. per 100 cc. was -90.9 , which agrees with the recorded value for fructose at this concentration and temperature.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY,
UNITED STATES DEPARTMENT OF AGRICULTURE.]

A FOURTH CRYSTALLINE PENTACETATE OF GALACTOSE AND SOME RELATED COMPOUNDS.

By C. S. HUDSON AND J. M. JOHNSON.

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The method of preparation of the second pentacetate of galactose by heating the first pentacetate with acetic anhydride and a trace of ZnCl_2 ¹ furnishes an indication that the two isomers are an alpha and beta pair, because this method of rearrangement changes the beta acetates of glucose, mannose, lactose, cellose, maltose and xylose to the corresponding alpha acetates. We have now sought to transform in similar manner the third pentacetate of galactose, which one of us recently found in the mother liquors of the preparation of the first pentacetate,² into an isomeric form, and we find that there is produced a fourth crystalline pentacetate of galactose having properties quite distinct from those of the three known isomers.

Rearrangement of the Third Galactose Pentacetate to a Fourth Form.

—A supply of 135 g. of the third pentacetate was obtained along with 940 g. of the first pentacetate by the acetylation of one kilo of pure galactose, according to the previously published directions. The specific levorotation of the recrystallized pure third form in benzene was -43.6 in 10% solution, in 99.5% glacial acetic acid -42.4 in 10% solution, both these values being near that reported previously for chloroform solution, -41.6 .

On combustion 0.2003 and 0.1987 g. subs. gave 0.3622 and 0.3595 g. CO_2 , and 0.1046 and 0.1020 g. H_2O .

Found: C, 49.32 and 49.34%; H, 5.84 and 5.74%. Theoretical: 49.21 and 5.68% for a galactose pentacetate.

Twenty-five grams of this third pentacetate dissolved to 100 cc. with acetic anhydride were heated with 2.5 g. ZnCl_2 on the steam bath until the specific rotation changed from its initial value of -41 to the constant rotation -16 , which required less than fifteen minutes. On pouring the solution into water a crystallization of some unchanged third pentacetate took place. The water was extracted with chloroform, the extract was washed with NaHCO_3 solution and with water, dried with CaCl_2 , and the chloroform evaporated. From the sirup, crystals of the third

¹ Hudson and Parker, *THIS JOURNAL*, 37, 1589 (1915).

² Hudson, *Ibid.*, 37, 1591 (1915).

pentacetate were again obtained, but the mother liquor from them yielded after a few days crystals of a different appearance, which were recrystallized from 95% alcohol, and were found to melt at 87° and to show a specific dextrorotation of +61 in chloroform. The yield was only 2.5 g. Analysis proved the substance to be a pentacetate of galactose.

On combustion 0.2074 and 0.2355 g. subs. yielded 0.3766 and 0.4248 g. CO₂, and 0.1038 and 0.1209 g. H₂O.

Found: C, 49.52 and 49.20%; H, 5.60 and 5.74%. Theoretical: 49.21 and 5.68% for a galactose pentacetate.

Mol. wt. (benzene soln. by f. p. method) gave values between 341 and 365. Theoretical 390.

The saponification of two half-gram portions of the substance by boiling three hours with 0.25 *N* H₂SO₄ gave values of 54.73 and 55.11% CH₃CO, the calculated value for galactose pentacetate being 55.13. The saponification of the substance with alcoholic potash yielded crystalline galactose which was identified by its specific rotation.

A comparison of the values found for the melting point and specific rotation in chloroform of this galactose pentacetate with those of the three known pentacetates leaves no doubt that the substance is a fourth isomer.

First galactose pentacetate, m. p. 142°, $[\alpha]_D = +23$; second galactose pentacetate, m. p. 96°, $[\alpha]_D = +107$; third galactose pentacetate, m. p. 98°, $[\alpha]_D = -42$; fourth galactose pentacetate, m. p. 87°, $[\alpha]_D = +61$.

After the preparation of a larger quantity of the fourth pentacetate and the recrystallization of the product from 95% alcohol until the rotatory power became constant the following specific dextrorotations were observed: $[\alpha]_D^{20} = +61.2$ in chloroform¹ (4.28 g. per 100 cc.), +60.6 in chloroform (10.12 g. per 100 cc.), +44.8 in benzene (3.52 g. per 100 cc.), +62.4 in 99.5% glacial acetic acid (3.04 g. per 100 cc.), and +70.2 in acetic anhydride (5.08 g. per 100 cc.). The substance is bitter in taste, very soluble in chloroform, benzene and glacial acetic acid, less soluble in alcohol and ether, and only slightly soluble in water. The crystals are colorless, transparent prisms sometimes a centimeter long.

The Equilibrium between the Third and Fourth Pentacetates.—Since the specific rotations in acetic anhydride of the third and fourth isomers are -41 and +70, respectively, and the constant equilibrium rotation in the presence of ZnCl₂, which acts as a catalyst of the reversible change, is -16, it appears that the third pentacetate makes up the greater part (77%) of the equilibrium mixture. This affords an explanation for the low yields (10%) in transforming the third into the fourth pentacetate and crystallizing the latter. On this view one would expect that the reverse transformation would be more readily accomplished and with a larger yield; experiment has verified this conclusion. The heating of

¹ *Chloroformum purificatum*, U. S. P.

1.27 g. of the fourth pentacetate in 25 cc. of acetic anhydride containing a little ZnCl_2 changed the specific rotation in fifteen minutes from $+70.2$ to the constant value -15.4 , and on pouring the solution into water and crystallizing in the usual way, a sufficient quantity of the third pentacetate was obtained (about 0.3 g.) to permit identification by its melting point and specific rotation.

Division of the Four Galactose Pentacetates into Two Pairs of Alpha and Beta Forms.—The reversible equilibrium in acetic anhydride solution containing ZnCl_2 , between the third and fourth pentacetates is entirely similar to the balanced reaction in this solvent between the first and second pentacetates. On the other hand, we have never noticed any indication that during either one of these reactions a member of the other pair was produced; in other words, the first and second isomers are interconvertible by direct rearrangement, likewise the third and fourth isomers, but the only way now known by which it is possible to pass from the first or second form to the third or fourth form, or *vice versa*, is by saponifying the chosen pentacetate and acetylating the resulting galactose with acetic anhydride and sodium acetate, under which conditions the first and third pentacetates are formed in admixture. These relationships may be accounted for by assuming that the four galactose pentacetates constitute two pairs of substances, the pairs differing by the position of the lactonyl ring, and the two members of each pair constituting the possible alpha and beta forms that must be assumed to exist for each ring position. On account of the fact that the first pentacetate is produced from galactose in large yield, while the third isomer is present only in small amount, it appears probable that the readily formed γ -ring is in the structure of the first and second pentacetates. The position of the ring for the third and fourth isomers is at present left undecided. Since the second isomer is more dextrorotatory than the first, it is to be considered the alpha form of that pair, and likewise the fourth isomer is the alpha form of the second pair. On this view the first and second pentacetates of galactose may be designated, respectively, as the *beta* and *alpha* forms of *pentacetyl γ -cyclo galactose*, and the third and fourth pentacetates as the *beta* and *alpha* forms of *pentacetyl (α , β , δ or η)-cyclo galactose*.

It has been suggested by the late J. U. Nef¹ that the alpha and beta pentacetates of glucose should be regarded as having different rings, rather than as being the possible alpha and beta forms of a common ring structure, probably a γ -ring. The data now at hand concerning the four pentacetates of galactose appear to us to show that the two glucose pentacetates must have the same ring because they pass readily one into the other in acetic anhydride containing ZnCl_2 .

¹ *Ann.*, 403, 331 (1914). The contrary view has been upheld by E. Fischer, *Ber.*, 47, 1980 (1914), and by Irvine, *J. Chem. Soc.*, 107, 524 (1915).

Since the ring formation remains fixed in these pentacetates of galactose, it is to be expected that each ring will give rise to a series of derivatives. Thus the acetochlorogalactose that has been prepared by Skraup and Kremann¹ from the first pentacetate is to be considered a γ -cyclo derivative, and there should exist a second acetochlorogalactose related to the third pentacetate by a common ring structure. Experiments are in progress in this laboratory for the purpose of correlating the derivatives of galactose with the two pairs of pentacetates, wherever possible, and the present opportunity is taken to record the preparation of three derivatives from the third galactose pentacetate, namely, the expected second form of acetochlorogalactose, a new tetracetyl galactose, and its phenylhydrazone.

A Second Acetochlorogalactose.—Twenty grams of the third galactose pentacetate were dissolved in 60 cc. dry chloroform and boiled two hours with 5 g. AlCl_3 and 13 g. PCl_5 , according to the method of Skraup and Kremann.² After washing with ice water and bicarbonate solution, and drying with CaCl_2 , the solution was distilled *in vacuo* to a sirup which crystallized on the addition of absolute ether. After several recrystallizations from ether, 11.6 g. of crystals were obtained which did not change in specific rotation on further crystallization. They melted at 67° (corr.). Chlorine estimations were made by dissolving the substance in alcohol and adding a solution of AgNO_3 in 50% alcohol.

0.2184 and 0.5681 g. substance (dried over H_2SO_4 in a desiccator) gave 0.0840 and 0.2200 g. AgCl , respectively.

Found: 9.51 and 9.57% Cl. Theoretical: 9.67% for a tetracetylchlorogalactose.

The substance is strongly levorotatory in chloroform: 6.2 g. per 100 cc. chloroform³ solution read -9.85 circular degrees in a 2 dcm. tube, hence $[\alpha]_D^{20} = -79.1^\circ$; 3.96 g. per 100 cc. read -6.10° , hence $[\alpha]_D^{20} = -77.1^\circ$. The previously known acetochlorogalactose was reported by Skraup and Kremann to be strongly dextrorotatory, $+213$ in chloroform. It appears, therefore, that the substance which we have prepared is an isomeric acetochlorogalactose having the same ring as exists in the third and fourth pentacetates.

A Third Tetracetate of Galactose and Its Phenylhydrazone.—Two isomeric tetracetates of galactose are recorded in the literature. One, which will be here designated the first tetracetate, was prepared by Skraup and Kremann⁴ from the first known form of acetochlorogalactose (γ -cyclo), and found to melt at 145° and to have the specific dextrorotation $+137$ in chloroform. The other tetracetate, here designated the second form,

¹ *Monatsh.*, 22, 375 (1901).

² *Ibid.*, 22, 379 (1901).

³ *Chloroformum purificatum*, U. S. P.

⁴ *Monatsh.*, 22, 1045 (1901).

was prepared by Unna¹ from acetobromogalactose (γ -cyclo) and found to melt at 102° and to have the specific dextrorotation $+71$ in water. The preparation of these tetracetates from the acetohalogen galactoses is proof that the free hydroxyl group has the position of the halogen atom, namely, on the end lactonyl carbon. Since both tetracetates are derived from γ -cyclo galactose derivatives, they may be considered as forming an alpha and beta pair in that series, the first tetracetate being α -tetracetyl γ -cyclo galactose and the second the beta form.²

Starting with the third galactose pentacetate, we have prepared a crystalline tetracetate which has entirely different properties from those of the two known tetracetates, and is accordingly designated the third isomer. Twenty grams of the third pentacetate were dissolved in 25 cc. acetic anhydride, the solution was cooled in an ice bath, 75 cc. of a saturated solution of HBr in acetic acid were added and the mixture allowed to stand ice cold ten minutes. Chloroform was then added, and the solution was washed in the usual way for the preparation of the acetohalogen sugars, with bicarbonate solution and water. The chloroform solution was then dried with CaCl_2 and evaporated. The sirup which remained could not be brought to crystallization, but its method of preparation and its subsequent conversion to the new tetracetate indicate that it is a bromoacetyl derivative of the third pentacetate. Fifteen grams of this sirup, dissolved in 150 cc. methyl alcohol, were shaken with 15 g. dry, freshly prepared Ag_2CO_3 until the solution gave no bromine reaction, the solution was filtered and evaporated to a sirup, which crystallized after a few weeks yielding 4.9 g. A larger quantity of the crystals were then prepared in the same manner and recrystallized from methyl alcohol until the specific rotation became constant. The substance proved to be a third tetracetate of galactose.

On combustion 0.1762 and 0.1803 g. subs. yielded 0.3126 and 0.3194 g. CO_2 , and 0.0936 and 0.0937 g. H_2O .

Found: C, 48.35 and 48.31%; H, 5.94 and 5.82%. Theoretical: 48.25 and 5.79% for a galactose tetracetate.

An acetyl determination made by boiling 0.3349 g. substance with 100 cc. 0.25 normal H_2SO_4 three hours in a quartz flask gave 50.2% CH_3CO , and a second analysis, using 0.2817 g. substance, gave 50.4%. Theoretical for a galactose tetracetate, 49.4%.

Saponification of 2 g. of the substance with alcoholic potash gave a yield of 90% of the theoretical amount of pure galactose, which was identified by its reducing power and specific rotation.

¹ *Inaugural Dissertation*, Berlin, 1911, p. 22.

² It may be mentioned in confirmation of this view that Dr. E. Yanovsky has recently correlated the first and second tetracetates with the alpha and beta forms of pentacetyl γ -cyclo galactose, respectively, by acetylating the tetracetates at low temperature in pyridine solution with acetic anhydride. Publication will be made later.

The following specific rotations of the pure tetracetate in different solvents were found, using a 2 dcm. tube: in chloroform¹ solution $[\alpha]_D^{20} = -17.8$ (4.7 g. per 100 cc.), in benzene -23.4 (3.5 g. per 100 cc.), in 99.5% glacial acetic acid -11.0 (4.1 g. per 100 cc.), in ethyl alcohol -6.2 (4.4 g. per 100 cc.), and in water -12.9 (4.4 g. per 100 cc.). The substance shows mutarotation. Thus the specific rotation in chloroform gradually changed at room temperature from its initial value -17.8 to -6.9 in one day, -3.1 in six days, and -1.9 in three months. An aqueous solution changed in specific rotation from -12.9 to $+21$ in four months.

Fehling's solution is readily reduced by the tetracetate. The melting point of the pure substance is $71-73^\circ$ (corr.).

By the acetylation of 1 g. of the tetracetate with acetic anhydride and sodium acetate 0.6 g. of the crystalline third pentacetate of galactose was obtained, which was identified by its melting point and specific rotation. This conversion proves that the ring in the pentacetate structure is not changed during the transformation through the bromoacetyl compound to the tetracetate. Since the tetracetate shows mutarotation towards increasing dextrorotation, it is to be regarded as the beta form.

A crystalline phenylhydrazone of the new tetracetate was prepared through the interaction of seven g. of the tetracetate and 5 cc. phenylhydrazine in ether solution. Two estimations of nitrogen in the crystals gave 6.68 and 6.61%, in comparison with the theoretical value of 6.41% for a tetracetyl galactose phenylhydrazone. The substance melted at 95° and showed a specific dextrorotation of $+15.5$ in chloroform.

WASHINGTON, D. C.

THE METHYL ESTER OF ORTHOBENZOYL-BENZOIC ACID.

By T. C. MCMULLEN.

Received April 20, 1916.

Plascuda² described the methyl ester of *o*-benzoyl-benzoic acid and Haller and Guyot,³ later, prepared it in five different ways, one of which was by the action of methyl alcohol on the acid chloride prepared from phosphorous pentachloride. In each case they obtained the same ester as described by Plascuda (m. p. $51-52^\circ$).

Meyer⁴ prepared the ester by the action of methyl alcohol on the acid chloride. The acid chloride was prepared in three ways: By (a) thionyl chloride, (b) phosphorus pentachloride, and (c) phosphorous trichloride. In the second case he obtained the ester already described, but in the other

¹ *Chloroformum purificatum*, U. S. P.

² *Ber.*, 7, 987 (1874).

³ *Bull. soc. chim.*, [3] 25, 54 (1901).

⁴ *Monatsh.*, 25, 475 (1904).

two experiments he obtained an isomeric ester whose melting point was about 80° . He inferred that the acid chloride in (a) and (c) is an isomer of that in (b).

As Martin¹ has shown that the acid chloride prepared by thionyl chloride is identical with that prepared by phosphorus pentachloride, it seemed worth while to repeat Meyer's preparation of the esters.

In each case the acid chloride was prepared as described by Meyer, and was usually obtained in the crystalline form. It was then added to excess of methyl alcohol in which it dissolved with evolution of hydrogen chloride. After about half an hour the solution was poured into dilute sodium bicarbonate solution and an oil separated which solidified after standing for some hours. It was found that the oil solidified sooner if it were not extracted with chloroform as recommended by Meyer. The solid was recrystallized by dissolving in methyl alcohol and adding water till the precipitate began to appear.

Experiment 1.—The acid chloride was prepared by using thionyl chloride and obtained in the crystalline form as described by Martin. The yield of ester was about 90%; m. p. 51.5° .

Calc. for $C_{15}H_{12}O_4 \cdot CH_3O$: 12.9. Found: 12.7, 12.8.

As Meyer obtained some of the low melting ester when he removed the thionyl chloride as completely as possible, but prevented this by using the acid chloride in presence of thionyl chloride, this experiment was repeated using the solution of the acid chloride in the thionyl chloride but the same product was obtained with no trace of Meyer's ester.

Experiment 2.—The acid chloride was prepared from phosphorus pentachloride and used in the crystalline form. The ester melted at 51.7° .

Experiment 3.—The acid chloride was prepared from phosphorus trichloride and, as it was not entirely freed from phosphorus trichloride and phosphorous acid, was not in the solid form. The ester was identical with that obtained in the two previous cases.

In each of the three preparations the product was subjected to fractional crystallization and no trace of another ester was found except in one instance where the acid chloride had been dissolved in ether. This product contained some ethyl ester melting at 58° .

Summary.

1. Meyer's preparation of the methyl ester of *o*-benzoyl-benzoic acid has been repeated using the acid chloride prepared in three different ways as described by him. No trace of the ester with the higher melting point was found.

2. Martin's conclusion that the *o*-benzoyl-benzoyl chloride prepared

¹ THIS JOURNAL, 38, 1142 (1916).

from thionyl chloride is the same as that prepared from phosphorus pentachloride is confirmed, and it is shown that the acid chloride prepared from phosphorus trichloride is identical with the others since it gives the same methyl ester.

These experiments were carried out under the direction of Professor F. B. Allan.

UNIVERSITY OF TORONTO.

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF THE HAWAII AGRICULTURAL EXPERIMENT STATION.]

ON THE DETERMINATION OF SMALL QUANTITIES OF HYDROCYANIC ACID.

By MAXWELL O. JOHNSON.

Received April 10, 1916.

In connection with some recent chemical work on cassava, there developed a need for a rapid and accurate method for the determination of small quantities of hydrocyanic acid. The silver gravimetric method is not suitable for small amounts of cyanides, such as one milligram, and the reducing substances found in plant distillates interfere with this and the various titration methods. These reducing substances also interfere with the picric acid colorimetric method of Waller¹ as shown by Chapman.²

Moore³ determines the hydrocyanic acid in cassava by heating 540 grams of pulped root in an iron retort for two hours, absorbing in potassium hydroxide solution the hydrocyanic acid distilled. The distillate is acidified with sulfuric acid and redistilled into water containing 5 cc. of tenth-normal potassium hydroxide. As the distillation proceeds, the distillate is titrated with tenth-normal silver nitrate and potassium hydroxide added as necessary, to provide for a minimum excess of potassium hydroxide present when the titration is completed. The method appears accurate but requires special iron retorts and a long distillation. The writer found when cassava was distilled into potassium hydroxide solution, that organic matter passing over colored the distillate yellow or orange. On adding an excess of sulfuric acid and redistilling into potassium hydroxide solution, organic matter again passed over. This interfered with the silver nitrate titration.

Various studies have been made of the Prussian blue colorimetric method, by Berl and Delpy⁴ by Lander and Walden,⁵ by Vorländer,⁶ by Knight,⁷

¹ *Proc. Roy. Soc. (B)*, **82**, 574 (1910).

² *The Analyst*, **35**, 471 (1910); **36**, 269 (1911).

³ Cassava, U. S. Bur. Chem., *Bull.* **106**, 12.

⁴ *Ber.*, **43**, 1430 (1910).

⁵ *The Analyst*, **36**, 266 (1911).

⁶ *Ber.*, **36**, 181 (1913).

⁷ *J. Ind. Eng. Chem.*, **6**, 909 (1914).

and by Viehoveer and Johns.¹ In this method, the cyanide solution must be concentrated to a very small volume and reagents added proportional to the amount of cyanide present to secure the maximum density of color.

The thiocyanate method of Francis and Connell² was investigated. In their method, they add 50 cc. of concentrated sulfuric acid to 50 g. of sample and 200 cc. of water in a liter distilling flask and distil about 150 cc. into 50 cc. of a 4% solution of potassium hydroxide. The distillate is made up to 250 cc. and to an aliquot of 50 cc. is added 1 cc. of yellow ammonium sulfide. The aliquot is evaporated to dryness on the water bath, taken up with 10 to 15 cc. water and barely acidified with hydrochloric acid. The sulfur is filtered off and one-half cc. of dilute hydrochloric acid added. The solution is boiled five minutes and filtered, and the boiling and filtering continued until the solution is absolutely clear. It is then made up nearly to the mark in a 50 cc. Nessler tube and 15 drops of 5% ferric chloride solution is added. The red color is matched with diluted portions of a standard solution containing potassium thiocyanate equivalent to 1 mg. of potassium cyanide per cc.

Discussion of the Francis and Connell Method.—The equilibrium of the reaction between a thiocyanate and ferric chloride is easily disturbed by any factor influencing the ionization of the reacting substances. A few experiments will show the influence of the presence of potassium chloride and of hydrochloric acid. One cc. of the standard thiocyanate solution was made up in Nessler tubes in various concentrations of potassium chloride or of hydrochloric acid, 15 drops of 5% ferric chloride were added, and the color was matched with the standard solution. The results are shown in Table I and by the curves in Fig. 1.

TABLE I.

Influence of Potassium Chloride and Hydrochloric Acid on the Thiocyanate Color.

Conc. HCl.	Color equivalent in cc. of standard.	Conc. HCl.	Color equivalent in cc. of standard.	Conc. HCl.	Color equivalent in cc. of standard.
10%	0.3	5%	0.35	0.1	1.6
5	0.4	4	0.45	0.5	1.7
2	0.45	3	0.55	0.01	1.5
1.3	0.5	2	0.7	0.005	1.4
1.0	0.6	1	0.8	0.001	1.2
0.5	0.7	0.5	1.0	0.0005	1.1
0.1	1.0	0.3	1.3		

The curve in Fig. 1 shows the great influence of the concentration of hydrochloric acid on the thiocyanate color. Small amounts of acid increase the color but increasing quantities of acid decrease the color, as do increasing quantities of potassium chloride. Yet Francis and Connell

¹ THIS JOURNAL, 37, 601 (1915).

² *Ibid.*, 35, 1624 (1913).

say to add one-half cc. of dilute hydrochloric acid in excess, not specifying the strength of the acid. They state,¹ "If too much acid is present, the solution will be lemon-yellow. If alkaline, the iron will be precipitated." The solution to be compared with the standard will contain 1.06% po-

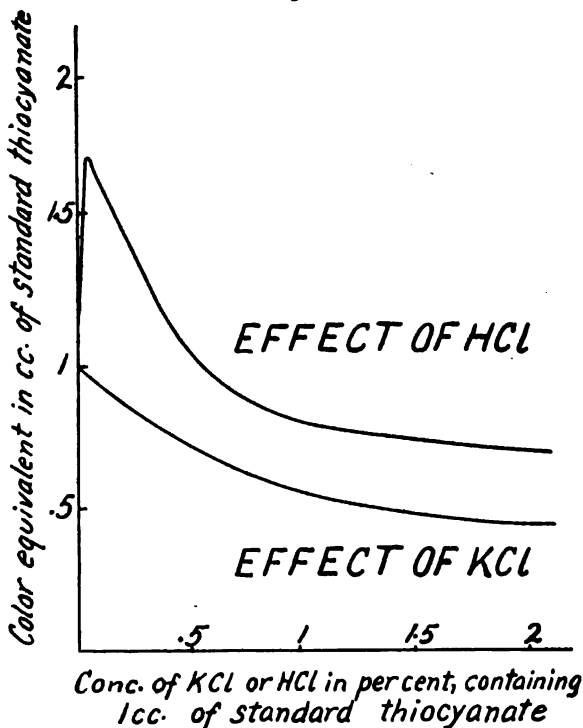


Fig. 1.—Curves showing the effect of potassium chloride and hydrochloric acid on the thiocyanate color.

acid and potassium chloride. A difference of five degrees in temperature made little appreciable difference in the color. If solutions to be compared are both at room temperature, the temperature factor should not affect results.

As shown by Viehoveer and Johns² a volatilization of some of the free thiocyanic acid took place on long boiling but the loss was found to be small. When a solution containing 3 cc. of the standard thiocyanate was boiled vigorously under the condition of the method for ten minutes, less than 0.2 cc. was lost.

Fair results were obtained by the Francis and Connell method by adding to the standard thiocyanate hydrochloric acid and potassium chloride equal to that in the solution to be compared, but the removal of the sulfur

tassium chloride and 0.1% of hydrochloric acid, if the one-half cc. of dilute acid added in excess was of 10% strength. One cc. of thiocyanate in these concentrations of acid and potassium chloride matched in color 1.3 cc. of the standard. Francis and Connell state that there is a tendency toward high results in their method and this is probably the cause.

The influence of temperature on the thiocyanate color was investigated. An increase in temperature increases the color of the thiocyanate alone, but decreases it in the presence of hydrochloric

¹ *Loc. cit.*

² THIS JOURNAL, 37, 601 (1915).

in the method is a tedious process. It is believed that the following method will be found convenient and accurate.

Description of the Method.

Distil the hydrocyanic acid from the sample into potassium hydroxide solution after adding sulfuric acid according to the Francis and Connell¹ method or after enzyme hydrolysis. To 50 cc. of the solution containing 0.1 to 8 mg. of potassium cyanide add 1 cc. of yellow ammonium sulfide and evaporate to dryness on the water bath. To the residue add 10 cc. of acetone and rub with a small glass or porcelain pestle to effect thorough extraction. Pour off the acetone into a small evaporating dish and repeat the extraction twice. Evaporate the combined acetone extracts to dryness on the water bath. Remove the dish and allow to cool to room temperature. Take up the residue in water, make up to 50 cc. in a Nessler tube and add 2 cc. of 0.5% ferric chloride solution. Match the color with standards made by diluting various quantities of a solution containing potassium thiocyanate equivalent to one milligram of potassium cyanide per cc. Mix the ferric chloride well with the solution before comparing. If the distillate is colored by organic matter and also the acetone extract, the following procedure should be adopted:

After evaporating the combined acetone extracts to dryness, take up the residue in 15 cc. of water and pour into a small separatory funnel. Wash the dish with two 5 cc. portions of water, pouring the wash water into the funnel. Add to the funnel 25 cc. of ethyl acetate which has previously been extracted several times with water to remove any soluble impurities. Shake well and allow to settle. The yellow color will be taken up by the ethyl acetate. Drain off the clear water solution into an evaporating dish and evaporate to dryness. Take up in water, make up to 50 cc. in a Nessler tube and compare with standard as usual.

Discussion of the Method.—Potassium thiocyanate is very soluble in acetone, while potassium hydroxide and potassium sulfide will not dissolve. To test the completeness of the acetone extraction, 1 cc. of yellow ammonium sulfide was added to each of two potassium hydroxide solutions containing 8 mg. of potassium cyanide. No. I was evaporated to a thick paste, No. II to dryness. The residues were extracted as in the method with five 10-cc. portions of acetone, but the acetone extracts were evaporated separately to dryness, and the thiocyanate and its potassium cyanide equivalent determined in each. The results are given in Table II.

When the solution is evaporated to a thick paste, the acetone dissolves the thiocyanate slightly better, but much less organic matter is taken up by the acetone when evaporated to dryness. Acetone of technical purity was used with good results.

¹ THIS JOURNAL, 35, 1624 (1913).

TABLE II.
Test of Completeness of the Acetone Extraction.
Potassium cyanide in mg. in thiocyanate extracted.

No. of extract.	Potassium cyanide in mg. in thiocyanate extracted.	
	I.	II.
1.....	7.5	7.3
2.....	0.5	0.7
3.....	Trace	Trace
4.....	None	None
5.....	None	None

To test the ethyl acetate extraction, 8 cc. of the standard thiocyanate solution were made up to 25 cc. and extracted with 25 cc. of washed ethyl acetate. The thiocyanate in the water solution was determined as usual and matched in color 8 cc. of the standard. The ethyl acetate was washed with three portions of 25 cc. water and the thiocyanate in each determined. The first portion showed a faint trace, less than 0.1 cc. of the standard, and the second and third showed no thiocyanate present. The yellow color due to organic matter will usually be removed by one extraction with ethyl acetate, but, if not, further extractions will leave the thiocyanate solution colorless. If the ethyl acetate extraction is used, the solution should be matched with the standard soon after adding the ferric chloride, since water extracts of ethyl acetate, after adding ferric chloride, give a yellow color on long standing.

The thiocyanate color is proportional to the amount of ferric chloride added. Since the range of potassium cyanide to be determined lay between 0.1 and 8 milligrams, 2 cc. of 0.5% ferric chloride were added as giving the greatest color change between these limits. The method can be adapted to quantities of cyanide greater or less than these limits by adding less or greater quantities of ferric chloride to the solution and to the standard.

To determine the accuracy of the method as a whole, solutions of about 1% potassium hydroxide were made up and to these were added quantities of a standardized potassium cyanide solution corresponding to 8, 6, 4, 2 and 1 milligrams of potassium cyanide. The potassium cyanide in these solutions was determined according to the method, both with and without the extraction with ethyl acetate, and the results agreed exactly with the theoretical.

A difference in thiocyanate color can be distinguished as follows: 0-4 cc. of standard, 0.1 cc.; 4-8 cc. of standard, 0.2 cc.

Summary.

(1) It has been shown that modifications are necessary in the Francis and Connell¹ thiocyanate method for the determination of small quantities of hydrocyanic acid and a modified method has been indicated.

¹ THIS JOURNAL, 35, 1624 (1913).

(2) A convenient and accurate method has been given for the determination of small quantities of hydrocyanic acid by the thiocyanate method, the potassium thiocyanate being leached out by means of acetone.

(3) Organic coloring matter can be removed from the thiocyanate solution by extraction with ethyl acetate.

HONOLULU, HAWAII.

THE SOLUBILITIES OF SEVERAL SUBSTANCES IN MIXED NONAQUEOUS SOLUTIONS.

BY J. W. MARDEN AND MARY V. DOVER.

Received January 19, 1916.

Introductory and Historical.—It is pretty generally agreed that the solubility of materials in mixed solvents is not as great as in one or other of the pure solvents. Mixtures of nonaqueous liquids are not infrequently recommended, however, for solution and separation. For example, the United States Pharmacopeia suggests the use of ether-chloroform for the extraction of quinine. Thorpe¹ suggests its extraction by means of a benzene-chloroform solution. In some cases the second solvent is used for the purpose of excluding undesirable materials. This can scarcely always be the case.

The solubilities of a number of substances have been determined in mixed aqueous solutions and a number of irregularities noted. The solubility of acetanilide,² for instance, has been shown to be greatest in 90% ethyl alcohol at 25°. If the concentration of the alcohol is either increased or decreased, the solubility is lowered. According to Müller,³ the solubility of strychnine at 20° in water is 0.021 g. strychnine per 100 g., while in ether it is 0.0342 g. In water saturated with ether the solubility is 0.0166 g., which value is lower than in either solvent.

Dunkelski⁴ has determined the solubilities of certain mercuric salts in given mixed nonaqueous solvents at different temperatures in an effort to show that chemical combination takes place between the solvent and solute in molecular proportions, much as we have the formation of hydrates in aqueous solution.

Bruner⁵ has determined the solubilities of iodine in various mixed solutions of nonaqueous solvents. Bruner's work shows that the solubility of iodine is less than proportional to the percentage composition of the solvent. The curves given in his paper are not smooth, but there are no very sharp breaks which might indicate the presence of various solution

¹ "Dictionary of Applied Chemistry," Vol. V, p. 677, Longmans, Green & Co., New York.

² Holleman and Antusch, *Rec. trav. chim.*, 13, 293 (1894).

³ *Apoth. Ztg.*, 18, 258 (1903).

⁴ *Z. anorg. Chem.*, 53, 327 (1907).

⁵ *Z. physik. Chem.*, 26, 145 (1898).

compounds. Bruner gives an arbitrary formula by which he calculates the solubility of the iodine. In some cases the calculated values are very far from even approximating the observed values. He acknowledges that the temperature conditions under which his work was done were not carefully regulated.

This paper is the result of the first portion of a larger piece of work now under way to furnish some accurate data on the solubility of certain substances in mixed nonaqueous solvents, and to answer some of the questions resulting from a study of the meagre literature now existing on the subject.

Theoretical Considerations.—It has been shown algebraically¹ that the fractional precipitation of substances follows the same general law as Bunsen's law for the washing of precipitates. If Bunsen's law is stated in terms of a fraction, the quantity of material which it is desired to remove still clinging to the precipitate, bears a constant ratio to the amount which is removed by each successive portion of wash liquid, provided that the quantity of wash liquid is always the same in each operation. When C_1 , C_2 , C_3 , etc., represent the weights of undesirable material remaining with the precipitate, after 1, 2, 3, etc., washings, the law can be expressed in the following manner:

$$\frac{C - C_1}{C} = \frac{C_1 - C_2}{C_1} = \frac{C_2 - C_3}{C_2} = K$$

When stated in this way, K represents the fraction of the total material (before the operation) which is removed by a given portion of wash liquid. It is evident, however, that if the expression gives a constant, the expression

$$\frac{C - C_1}{C_1} = \frac{C_1 - C_2}{C_2} = \frac{C_2 - C_3}{C_3} = K$$

should also give a constant (or nearly a constant) which has a somewhat higher numerical value.

The constant of distribution between two immiscible solvents is usually expressed in the latter way, in order to show the equilibrium relationship between the concentrations of the solute in the two solvents.

The value of K in the fractional expression $\frac{C - C_1}{C} = \text{etc.}$, has been calculated in the first four tables of results for each 10% change of the composition of the solvent (where the mixed liquid is considered the solvent) using the values C , C_1 , C_2 , etc., as the differences between the observed solubilities and the solubilities in the poorer solvent. As this indicates, if K is a constant, it represents the fraction of the total precipitable material removed by any 10% change in the composition of the solvent.

¹ Blackman, *J. Phys. Chem.*, 13, 436 (1909).

When the percentage composition of the solvent is plotted against the solubility on the rectangular system, the curve is exponential in form. (Fig. 1a.—Acetanilide in chloroform-ether.) There are various ways in which the curves of a ternary system of this kind may be plotted.

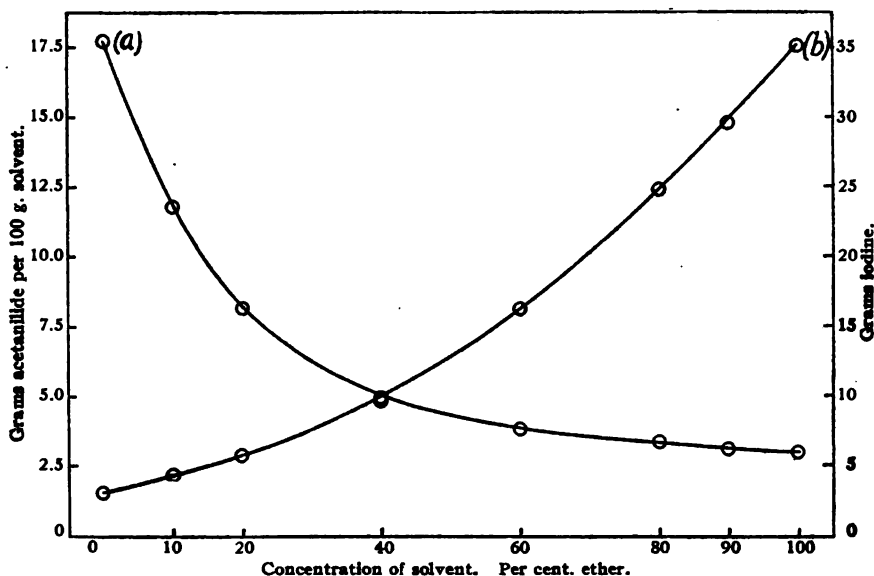


Fig. 1.

While the triangular system is convenient in many ways, the curves obtained by the rectangular system show the slope better for analytical purposes and for this reason are given here.

The fact that the curve is exponential in form may also be proved by applying the test of an exponential equation. If the $\log (C - C_1)$, $(C_1 - C_2)$, etc., is plotted against the $\log (1/C)$, $(1/C_1)$, etc., the result (Fig. 2a) is a straight line. It may also be seen from the slope of this curve that the exponent (n) is nearly equal to one. Two points have been disregarded here because the solubility change was less than 0.3 g. and the experimental error was consequently large.

If K is a constant, a formula can readily be developed by which the solubility for any percentage composition of solvent can be calculated from the average experimental value of K . Since K represents the fraction of the total amount of material (which may be precipitated by the poorer solvent) that is precipitated by any 10% portion of the poorer solvent, $(1 - K)$ represents the fraction still in solution. $(1 - K)^n$, then, represents the fraction of material still in solution after the addition of (n) 10% portions of the poorer solvent. If we let A equal the solubility in the better solvent and B equal the solubility in the poorer solvent,

the formula, by the use of which the solubility may be calculated, is as follows:

$$[(1 - K)^n (A - B)] + B = \text{Solubility}$$

As will be seen in the cases of acetanilide and strychnine in chloroform-ether solutions, this relationship holds fairly well. When benzoic acid and iodine were tried in the same way K was far from a constant. It was found, too, that the curves, though smooth, were different from those

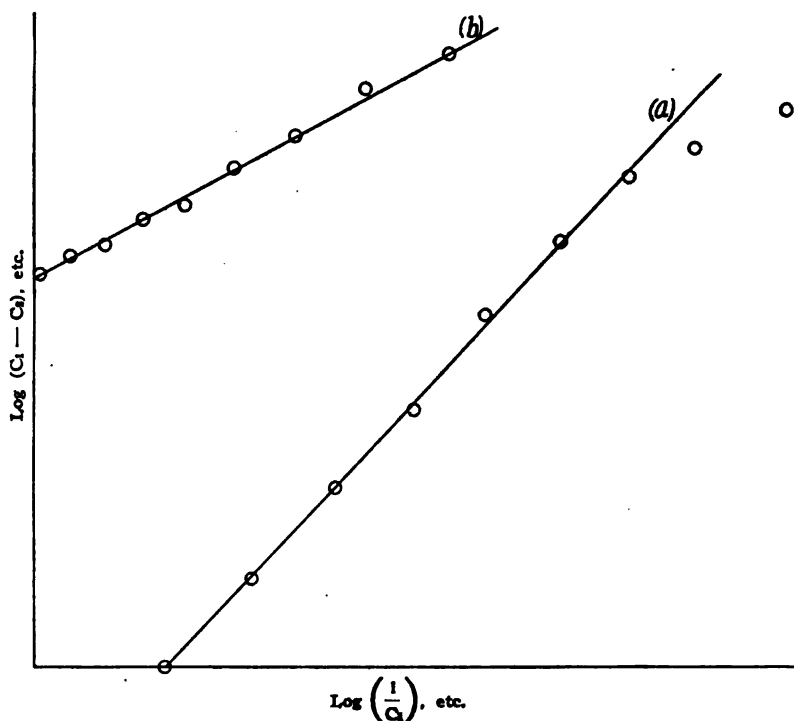


Fig. 2.

obtained before. (Fig. 1b.—Iodine in chloroform-ether solutions.) When the $\log (C - C_1)$, $(C_1 - C_2)$, etc., is plotted against the $\log (1/C)$, $(1/C_1)$, etc., however, a straight line is obtained (Fig. 1'2b), the exponent (n) equalling very nearly two. From this, the expression $\frac{(C - C_1)}{\sqrt{C}} =$, etc., should give a constant.

Other cases were found where the curves were broken, showing changes in the composition of the solute. The curves for acetanilide in acetone-benzene, benzoic acid in acetone-benzene and the same material in ethyl acetate-benzene solutions are given in Fig. 3a, b and c, respectively. No constant relationship could be developed to cover such curves.

Methods of Determination.—The solubilities as recorded in this paper were determined by shaking the mixed solvents with a large excess of the solid material for twelve to twenty hours in a thermostat, which regulated at 25° within one-tenth of one degree. The bottles had ground glass stoppers which were protected by a coating of beeswax and rosin, over which was tied a piece of rubber sheeting.

The saturated solutions were forced from the bottles upward with air pressure, through a glass-wool filter, into an especially constructed weighing pipet. This pipet is very similar to that described by Hall¹ but was in use before his publication. This type of pipet is not only convenient for weighing out such solutions, but if the small neck at the upper end of the apparatus be calibrated, the densities of the solutions can be determined in weighing out the liquids for the solubility determinations.

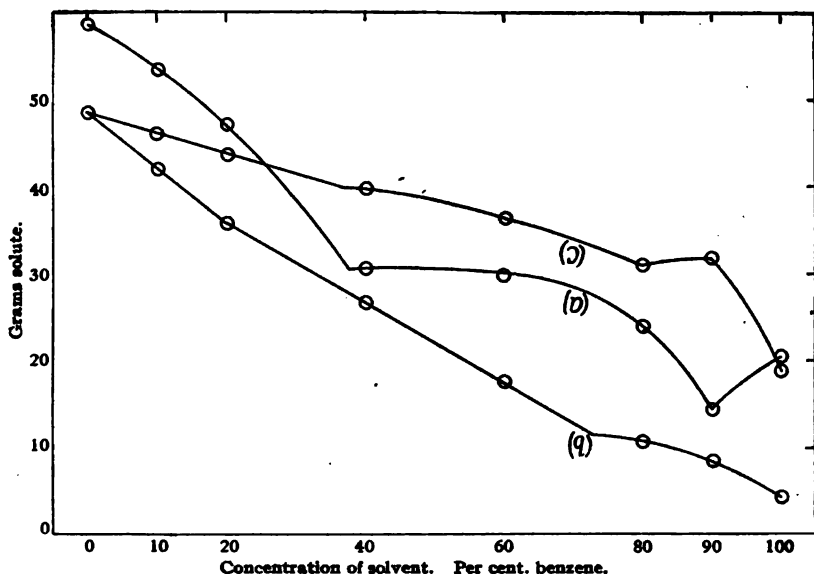


Fig. 3.

Most of the substances were determined by distilling off the solvent, drying in a sulfuric acid desiccator and weighing directly at ordinary temperatures. The iodine, however, was titrated immediately after having been weighed out, with carefully standardized sodium thiosulfate solution.

Purity of Materials.—The chloroform was Kahlbaum's best grade, the specific gravity of which was 1.479 at 25° . Linebarger² gives the specific gravity of pure chloroform at 25° as 1.4806. The ether was Merck's which had been distilled over sodium. It showed an average

¹ THIS JOURNAL, 37, 2062 (1915).

² *Am. Chem. J.*, 18, 442 (1896).

specific gravity of 0.709. Linebarger gives the specific gravity of ether at 25° as 0.7094. These solvents conformed in every respect to the tests for purity given by the United States Pharmacopeia and Krauch.¹

The ether-chloroform solutions which were carefully weighed together are listed below in terms of percentage by weight with the specific gravities of the solutions.

TABLE I.

No.	% chloroform.	% ether.	Sp. gr. at 25°.
1.....	100	0	1.479
2.....	90.04	9.96	1.342
3.....	79.8	20.2	1.225
4.....	59.7	40.3	1.047
5.....	40.8	59.2	0.915
6.....	19.8	80.2	0.797
7.....	10.2	89.8	0.752
8.....	0	100	0.709

The acetone-benzene solutions were made from the best purified material available. The specific gravities of these solutions together with their percentage compositions are given in Table II.

TABLE II.

No.	% acetone.	% benzene.	Sp. gr. at 25°.
1.....	100	0	0.792
2.....	90	10	0.800
3.....	80	20	0.808
4.....	60	40	0.824
5.....	40	60	0.841
6.....	20	80	0.857
7.....	10	90	0.866
8.....	0	100	0.876

The specific gravity of acetone is given by Saposchnikow,² D_4^{15} , as 0.79705. The specific gravity of benzene at 25° is given by Linebarger as 0.87661.

The specific gravities of ethyl acetate-benzene solutions are stated in the same way.

TABLE III.

No.	% ethyl acetate.	% benzene.	Sp. gr. at 25°.
1.....	100	0	0.896
2.....	90	10	0.894
3.....	80	20	0.892
4.....	60	40	0.887
5.....	40	60	0.883
6.....	20	80	0.879
7.....	10	90	0.8775
8.....	0	100	0.876

¹ "Testing of Chemical Reagents," D. Van Nostrand & Co., New York (1902).

² *J. Russ. Phys. Chem. Gesellschaft*, 28, 229 (1896).

The specific gravity of ethyl acetate is given by Linebarger as 0.89156 at 25°. There seems to be some difference between this value and the value obtained in this work. This sample showed a boiling point of 77.5° on a standardized thermometer. By a comparison with the values given by other authors for the specific gravity of this substance at several different temperatures, the value given by Linebarger appears to be somewhat low.

The acetanilide conformed to the standards of the U. S. P. Two grams of the material left no weighable residue when ignited. The melting point was 113°. The determination of the nitrogen by the Kjeldahl method gave a value within 0.02% of the calculated percentage.

The strychnine, in addition to the requirements of the U. S. P., was tested for other impurities which might be in such a sample. None were found. There was no weighable residue left by the ignition of 2 g. of strychnine. This sample gave a melting point of 284°.

The iodine, which was resublimed, showed no test for any of the impurities described by the U. S. P. or by Krauch. The iodine was further carefully tested quantitatively by titration with sodium thiosulfate solution which had been standardized by means of an especially prepared potassium dichromate solution. The average weight of iodine, calculated from the volume of thiosulfate solution, was almost exactly that taken for analysis and considerably below the errors of titration.

No impurity was found by the tests described in the U. S. P. for benzoic acid. The melting point was 122°. Weighed samples were dissolved in hot water and titrated with tenth-normal sodium hydroxide solution, using phenolphthalein in the hot solution; 0.2000 g. of the acid gave an average weight by titration of 0.2002 g.

It might be pointed out here, however, that even though quite pure, these reagents may vary a small amount in their content of certain objectionable materials and yet conform to our standards of purity. A small amount of water or alcohol, for example, may be present in some of the liquid solvents and escape detection, which may have a marked effect on the solubility of some substance in it. This may explain, partly, at least, why some of the solubility results obtained here do not in all cases check those of previous observers. As an example of such discrepancies, the case of mercuric chloride might be cited. Four authors¹ give its solubility at 25° varying from 22.2 g. to 40 g. per 100 g. of ethyl acetate. In acetone at the same temperature, also, the solubility varies from 37.4 g. to 61.7 g. per 100 g. of solvent.

The Solubility Data.—In stating the data, the solubility of the solid substance is given in terms of grams per 100 g. of the mixed solvent, the

¹ Seidell, "Solubilities of Inorganic and Organic Substances," D. Van Nostrand & Co., New York (1907).

percentage composition of the solvent being given. The results are listed in this way to show the decrease in solubility with the change in composition of the liquid mixture.

TABLE IV.
Acetanilide in ether-chloroform solutions at 25°.

Composition of solvent. % chloroform.	Observed solubility.	$K = \frac{C - C_1}{C}$	Calculated solubility.
100	17.7
90	11.7	0.405	12.2
80	8.2	0.398	8.8
(70)	(6.2)	0.378	6.5
60	4.95	0.378	5.1
(50)	(4.25)	0.341	4.3
40	3.8	0.333	3.8
(30)	(3.5)	0.333	3.46
20	3.25	0.417	3.26
10	3.05	...	3.13
0	2.9

Average..... 0.373

The values given in the above table in parenthesis have not been determined experimentally but read from curves (Fig. 1a). It will be noticed that K has a value that is very nearly constant. Speyers¹ has found the solubility of acetanilide in chloroform at 25° as 14.5 g. per 100 g. of the solvent.

TABLE V.
Strychnine in ether-chloroform solutions at 25°.

Composition of solvent. % chloroform.	Observed solubility.	$K = \frac{C - C_1}{C}$	Calculated solubility.
100	15.3
90	7.1	0.538	7.1
80	2.77	0.612	3.3
70	(1.5)	0.462	1.5
60	0.65	0.574	0.7
50	(0.35)	0.476	0.47
40	0.27	...	0.18
30	(0.21)
20	0.15
10	0.09
0	0.02

Average = 0.532

Only the first few values given here are calculated for K . The reason for this is that when the solubilities get much below 0.3 g. the error of determination becomes large. The solubility of strychnine in chloroform and in ether at 25° is given by Müller² as 16.6 and 0.0182 g. in 100 g. of solvent, respectively.

¹ *Am. J. Sci.*, [4] 14, 294 (1902).

² *Apoth. Ztg.*, 18, 258 (1903).

TABLE VI.
Benzoic acid in ether-chloroform solutions at 25°.

Composition of solvent. % chloroform.	Observed solubility.	$K = \frac{C - C_1}{C}$	$K = \frac{C - C_1}{\sqrt{C}}$
100	38.4
90	34.0	0.188	0.910
80	30.1	0.205	0.897
70	(26.6)	0.232	0.902
60	23.2	0.293	0.995
50	(20.8)	0.293	0.840
40	18.6	0.380	0.916
30	(16.8)	0.500	0.947
20	15.6	0.667	0.895
10	15.2	0.667	...
0	15.0

Average = 0.913

The solubility of benzoic acid in chloroform at 25° is given by Bourgoin¹ as 14.3 g. in 100 g. chloroform and 31.35 g. in 100 g. of ether. It will be noticed here how very nearly constant are the values of K in this table.

TABLE VII.
Iodine in ether-chloroform solutions at 25° (Fig. 1b).

Composition of solvent. % chloroform.	Observed solubility.	$K = \frac{C - C_1}{C}$	$K = \frac{C - C_1}{\sqrt{C}}$
0	35.1
10	29.6	0.172	0.973
20	24.8	0.181	0.932
30	(20.2)	0.212	0.990
40	16.3	0.230	0.934
50	(12.7)	0.272	0.992
60	9.83	0.299	0.925
70	(7.5)	0.342	0.900
80	5.73	0.402	0.843
90	4.31	0.539	0.877
100	3.10

Average = 0.931

Bruner gives the solubility of iodine in chloroform at about 15° as 3.02 g. per 100 cc. of solution. Molecular-weight determinations of iodine by the boiling-point method in ether indicate that it has a diatomic molecule.

Each set of data which has been given thus far, when plotted as in Fig. 1, gives smooth curves in which no breaks have been observed. It will be recalled that the values for acetanilide in ether-chloroform solutions give a constant for the simple relationship $K = \frac{C - C_1}{C}$. In acetone-benzene solutions, acetanilide gives a curve (Fig. 3a) not unlike the curves

¹ *Ann. chim. phys.*, [5] 13, 406 (1878).

obtained when the solubilities of certain hydrates are plotted against temperature. Two other cases where broken curves have been obtained are cited below.

TABLE VIII.

Acetanilide in acetone-benzene solutions at 25°.

Composition of solvent. % benzene.	Observed solubility.
0	39.4
10	45.7
20	36.0
30	(33.0)
40	30.5
50	(30.0)
60	29.2
70	(20.0)
80	13.0
90	6.78
100	1.36

TABLE IX.

Benzoic acid in acetone-benzene solutions at 25°.
(Fig. 3b.)

Composition of solvent. % benzene.	Observed solubility.
0	55.6
10	51.3
20	49.2
30	(47.0)
40	42.2
50	(37.0)
60	33.5
70	(31.0)
80	24.1
90	18.3
100	11.6

TABLE X.

Benzoic acid in ethyl acetate-benzene solutions at 25° (Fig. 3c.)

Composition of solvent. % benzene.	Observed solubility.
0	41.2
10	28.1
20	29.0
30	(26.5)
40	23.9
50	(22.0)
60	20.4
70	(20.0)
80	16.5
90	14.0
100	11.6

A glance at the curves shows that no such expressions could be used on this curve as were used to calculate K in the data above.

Conclusions.

1. The solubilities of several substances have been determined in nonaqueous solutions.

2. It has been found that the solubilities of substances tried in ether-chloroform are exponential functions of the percentage composition of the solvent. The law which governs the fractional precipitation may be stated, if so desired, in the same way as the law of distribution or Bunsen's law for the washing of precipitates.

More cases of this kind have been observed and will be given in a later contribution.

3. The curves show only one case where the solubility in mixed solvents is greater than in either of the pure liquids. This is the case of acetanilide in a solvent made up of 10% benzene and 90% acetone.

4. It has been pointed out that the molecular weight of iodine in ether at its boiling point corresponds to Formula I₂, and it is well known that the molecular weight of benzoic acid in certain nonaqueous solvents is not greater than that which would correspond to a double molecule. If the formula $K = \frac{C - C_1}{\sqrt{C}}$ is true in ether-chloroform solutions, however,

there must be a dissociation when the solid material is precipitated. The reason for this is the same reason that we use to explain the similar square-root relationship in the distribution of benzoic acid between benzene and

water.¹ It is quite unlikely that a substance going from solution to the solid form should dissociate. By analogy we should rather expect the reverse process.

The data for mercuric chloride, which are not given above because a small amount of moisture was found in the sample after the determinations were made, are interesting on this point. Mercuric chloride gives a normal molecular weight corresponding to the formula HgCl_2 by the boiling-point method in ether and yet the data show that the relationship $K = \frac{C - C_1}{\sqrt{C}}$ holds very closely.

We have no better explanation to offer at present than to say that perhaps solution compounds similar to the hydrates which we have in aqueous solutions are formed in some cases. These compounds are not stable, however, at the boiling point of the solvent any more than hydrates are at 100° and are decomposed when the solid material is precipitated by the addition of the poorer solvent.

Compounds of mercuric chloride and certain nonaqueous solvents have already been isolated by Dunkelski.²

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ON THE DIGESTIBILITY OF BREAD. I. SALIVARY DIGESTION IN VITRO.

[PRELIMINARY PAPER.]

By J. C. BLAKE.

Received March 14, 1916.

Summary.

The rate of digestion *in vitro* of the starch of bread can be followed readily and accurately by means of the polariscope, the only optically active substance entering the solution under the conditions herein stated being maltose. A rather large array of subsidiary findings surrounds this main observation, such as confirmation of the specificity of the starch of different plants, a clearer identification of some of the ingredients of the starch of the common cereals and the products of their hydrolyses (including two new substances), the variation of the activity of salivary amylase with the dilution and with the temperature, a comparison of amylases of different origin, and a comparison of the salivary digestibility of a number of standard breads. This paper is a report of progress rather than a finality.

¹ Nernst, "Theoretische Chemie," 483 (1903).

² *Loc. cit.*

Historical.

The statements of Maquenne and Roux¹ that in the digestion of amylose no considerable amounts of dextrans enter the solution, but that the dextrans ordinarily observed are derived from the amylopectin of starch are greatly at variance with the older ideas of Musculus and Gruber² and of Brown and Heron,³ still current in American works on physiological chemistry,⁴ according to which boiled starch is a homogeneous substance⁵ which gradually hydrolyzes by the continual splitting off of maltose or isomaltose, the residual nucleus passing successively through the stages of soluble starch, amyloextrin, erythroextrin, and an indefinite number of achroödextrans. So confusing is the literature of this subject, much of which is paraphrased in the works cited, that at the present time none of these ingredients has any standing as a pure chemical substance. On this account the polysaccharides recognized in this work are here defined anew, in close agreement with the general trend of past usage, the word dextrin in particular being applied only to substances markedly diffusible through membranes. The true process of salivary digestion seems to lie about half way between the two processes previously referred to.

Experimental.

Polysaccharides.—By working with the starch of bread, as well as with raw and boiled starch, the author was able to recognize more clearly a considerable number of polysaccharides which seem to be chemical individuals, although exhaustive study of each of them is yet to be made. It seems necessary and worth while to record these preliminary observations both for their own sakes and because they were used in indicating *pro tanto* by negation that only maltose was present in the solutions hereafter described.

Cellulose and Amylocellulose.—It should be emphasized that in bread pulp (the white interior of the loaf) the starch granules are not disrupted,⁶ and that very little of any soluble carbohydrate is present outside the granules, even though the starch is apparently as digestible as boiled starch (page 1256); whereas in boiled starch the granules are disrupted and, on long boiling (several hours) or by superheating, go completely

¹ Maquenne and Roux, *Ann. chim. phys.*, [8] 9, 179; Meyer and Jacobson, "Lehrbuch der Organischen Chemie," 1913, 1032; Hammarsten-Hedin (Mandel), "A Text-book of Physiological Chemistry," 1914, 229.

² *Z. physiol. Chem.*, 2, 177 (1878).

³ *Liebig's Ann.*, 199, 65 (1880).

⁴ Hawk, "Practical Physiological Chemistry," 1913, 61; Mathews, "Physiological Chemistry," 1915, 328.

⁵ Reichert, "Differentiation and Specificity of Starches in Relation to Genera, Species," etc., *Pub. Carnegie Inst. Wash.*, 1913, p. 160.

⁶ Jago, "The Technology of Bread-Making," 1911.

into solution. Hence the digestion of the cell walls is the more readily observable with starch from bread, making clear the differentiation of the substance composing the walls from the substances found within the granules. This substance we will call amylocellulose, because of its slow digestibility, the cell walls of the large granules of starch from bread becoming disrupted under ordinary conditions of salivary digestion *in vitro* only after more than 24 hours. After 48 hours the process is ended, except for a few chain-like cell fragments and the cell walls of a few very large hexagonal-shaped cells. This definition is at variance with that of Maquenne, who apparently confuses amylocellulose, amylose (the main constituent of cooked starch) and "reverted amylose" (the insoluble and indigestible substance which settles out of starch solutions on standing). Amylocellulose gives no color with iodine water, as may readily be determined by testing after the cell contents have been removed by digestion (*infra*). It probably hydrolyzes through the stage of maltose and constitutes about 10% of the starch granules (dried at 120°), as indicated by the increase in the polarization of the digestion mixture after the contents of the cells have been digested (that is, after four hours, Tables I and IV). The chain-like fragments and the walls of the hexagonal cells are probably cellulose. The interior of these latter cells stains yellow with iodine, indicating the presence of *protein*.¹ All of these features were later recognized in slightly boiled corn and rice starch (page 1257), indicating great similarity between freshly boiled starch and that of bread, and also that the indigestible cells were not derived from the yeast of the bread.

Amylopectin and Rose-amylose.—If raw cereal starch be treated with iodine water in minimal amount a red color is developed. This color disappears at approximately 46° and reappears at the same temperature provided sufficient iodine was originally added to turn the raw starch purple. The blue tint of the purple disappears during the heating owing to loss of iodine from the solution. The substance giving this red color with iodine is rose-amylose, first recognized by Day.² It is the substance responsible for most of the confusion existing with regard to the chemistry of starch, since it is usually mistaken for erythrodextrin,³ and has also been mistaken for "*residual dextrin*," as it is much less readily digested than the dextrins (*infra*). It disappears from ordinary digestion mixtures only after four hours. It is further sharply differentiated from erythrodextrin (*q. v.*) by the difference of 13° in the transition temperatures of these two iodides, by the much greater sta-

¹ Confirmed by digestion with pepsin.

² Day, "Digestibility of Starch of Different Sorts as Affected by Cooking," Univ. of Chicago Press, 1908, 37, 41; Reichert, *Loc. cit.*, p. 195.

³ Hawk, *Loc. cit.*, pp. 10, 65; Mathews, *Loc. cit.*, p. 899.

bility of its iodide toward alkalies and toward maltose. The iodide of rose-amylose disappears when the calculated alkalinity (using NaOH, Na_2CO_3 , or NH_4OH) reaches 0.1 *N*, whereas the iodide of erythroextrin disappears when the alkalinity reaches 0.005 *N*. The difference in the stability of these two iodides to maltose probably accounts for the order of appearance of these iodides and the common blue iodides of starch on the gradual addition of iodine-water to mixtures of these substances. The iodide of rose-amylose appears first, then the ordinary blue iodides, then that of erythroextrin. There is no rose-amylose in potato starch.

Rose-amylose is probably a product of the hydrolysis of amylopectin, the substance which gives a freshly-boiled cereal starch solution its excessive viscosity when cool. Addition of saliva to such a viscous solution or paste, which previously gave a blue color with minimal amounts of iodine-water, completely destroys the excessive viscosity within half a minute, making the mixture rich in rose-amylose. Arsenic acid of 0.05% or greater concentration (as As_2O_3) completely stops this change of amylopectin into rose-amylose; whereas the same acid at 0.005% lessens the time required for the disappearance of rose-amylose by more than one-half. Santesson¹ found this identical phenomenon in the activity of the catalytic enzyme of frog muscle. Dilute solutions of acetic, butyric and lactic acids facilitate this change but slightly, agreeing with the results recorded later on that the slight variation in the acidity of different samples of bread does not appreciably affect their rate of digestion. No concentration of these acids was found which completely prevents the change of amylopectin to rose-amylose. Hence 0.07% arsenic acid was used to stop all digestion, no other change seeming to take place as readily as this, or to take place at all in solutions containing this concentration of arsenic acid. The fate of rose-amylose is being investigated. It probably finally reaches maltose for the most part. The observation of Tanret² that the amylopectin contains all the phosphorus found in starch should be noted in this connection. A rough estimate of the amount of amylopectin in wheat starch can be made from the polarizations hereafter recorded showing about 10% of amylocellulose, 70% of amylose, and (by difference) 20% of amylopectin. This is in fair agreement with the estimate of Maquenne and Roux, who place the "amylose" (which we have seen includes amylocellulose) at 80-85%, the amylopectin at 15-20%.

Achroödextrin.—If bread or boiled starch digestion mixtures be filtered before the addition of iodine, the rose-amylose may readily be detected in the residue, but the filtrate ordinarily gives no color with iodine. Hence the theory of Maquenne and Roux, already cited, that no dex-

¹ *Skand. Arch. Physiol.*, 32, 405; *Chem. Abs.*, 9, 2097.

² *Bull. soc. chim.*, 17, 83 (1915).

trins are present. If, however, alcohol be added to the filtrate during the first few minutes under usual conditions, a white precipitate of achroodextrin forms when the alcohol reaches 72 to 80% by volume. Under the conditions of the experiments hereinafter described, a 1% bread suspension gave 0.04% of this dextrin at the end of five minutes, 0.01% at the end of ten minutes, and only a trace at the end of twenty minutes. These values are corrected for a slight precipitate due to the saliva under these conditions. After standing overnight, the dextrin was filtered out in a Gooch crucible, dried at 100°, weighed and redissolved in water. This solution indicated a specific rotation of 170 for this dextrin, a value which is recorded merely to show its properties as a dextrin, the amount worked with being too small to give an accurate result. Further addition of absolute alcohol to the filtrate from this dextrin gave no precipitate or opalescence. Commercial dextrin "precipitated by alcohol" gave 26% of this dextrin.

Maltose was rather sharply identified as follows: A 1.00% (final concentration) suspension of disintegrated bread (Table II), which gave a reading of about 0.1% on the polariscope, which read percentages of *d*-glucose directly, gave readings of about 1.0% within a few minutes after mixture with saliva in moderate amount. In the absence of maltase and proteolytic enzymes the readings slowly increased to about 1.30 (Table I), this slow increase registering for the most part the slow digestion of the rose-amylase and the amylocellulose. The initial rapid rise in the polarization seems to be due to the digestion of the main content of the starch granules (which we may call *amylose*), the optical activity after the digestion of the achroodextrin (first fifteen minutes) being due wholly to maltose. The absence of dextrans is indicated not only by the negative tests with iodine and absolute alcohol, but by the unbroken asymptotic curve (Fig. 1, for Bread No. 1, Table I). The absence of *d*-glucose in appreciable amounts is indicated by negative tests for glucosazone and with a modification of Barfoed's reagent (twice as much copper acetate being used as that ordinarily specified,¹ and the time of boiling being one-half minute), and also by comparison with results obtained when maltase was present (page 1258). A further

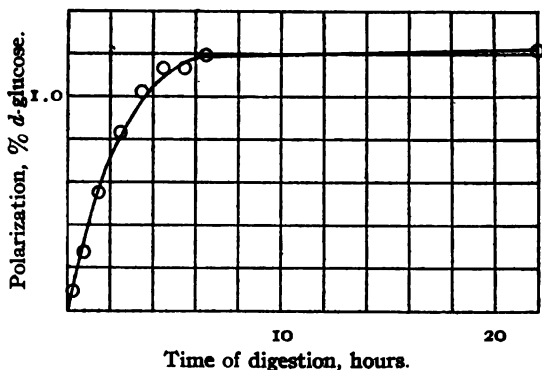


Fig. 1.

¹ Hawk, *Loc. cit.*, p. 443.

pseudo-quantitative proof that only maltose was present in the solutions referred to is the fact that on partial hydrolysis with acids they show the same change of optical activity as a solution of pure maltose having the same polarization. Thus when such solutions are heated half an hour in boiling water with 3% of concentrated hydrochloric acid (by volume), each loses one-third its optical activity. The difficulty of completely hydrolyzing maltose with acids, owing to the reversibility of the reaction, is well known.¹ Finally, the reading 1.30, read as *d*-glucose, corresponds to 0.47% starch, using the equations

$$\% \text{ Maltose} = \text{rotation as } d\text{-glucose} \times \frac{52.5}{138.3},$$

and

$$\% \text{ Starch} = \% \text{ maltose} \times \frac{324}{342},$$

in close agreement with the percentage of starch usually present in bread (50%²), and that indicated by the usual method of testing. (This bread contained 40.0% water and 8.0% gluten, besides salt and other minor ingredients.) Maltose shows little multirotation, and isomaltose from starch, if present, has the same specific rotation as maltose. In so far as the optical activity is due to maltose, multiplication of the readings recorded in the tables by 0.36 gives the percentage of the original material represented by the starch digested at the time the reading was made.

On this basis wheat No. 2, Table II (average of three samples), at the end of fifteen minutes (the time the achroödextrin disappears from the filtrate) showed a digestion of 72% of the estimated amount (0.50%) of starch present. Although maltase from the disintegrated bread was present in these experiments, as indicated by the subsequent decrease in the polarizations, yet the rate of such decrease is such that it would be negligible for the first fifteen minutes.

The complete, or nearly complete, change of starch into maltose has been claimed by Maquenne (*loc. cit.*) and by Fernbach and Wolff³ and others,⁴ as determined by copper reduction, polariscopic and other methods.

Erythrodestrin was clearly recognized as follows: Bread was digested in the presence of toluene with saliva diluted with 99 volumes of water. Under these conditions at the end of 15 minutes 60% of the total amount of starch present was found in the filtrate as erythrodestrin, as determined colorimetrically after the addition of arsenic acid and iodine-water. The amount of erythrodestrin in the digestion mixture gradually decreased, dis-

¹ Daish, *J. Chem. Soc. (Trans.)*, 105, 2053.

² Jago, *Loc. cit.*, p. 540.

³ *Compt. rend.*, 145, 80.

⁴ Syniewski, *Liebig's Ann.*, 324, 214.

appearing at the end of two hours. The standard erythro-dextrin solution for colorimetric comparison was prepared from a white commercial "Dextrin, Precipitated by Alcohol," which contained only a trace of insoluble matter and of amylo-dextrin (*infra*), by precipitating the erythro-dextrin with 65% alcohol (final concentration). The erythro-dextrin began to precipitate when the concentration of the alcohol reached 50%; but achroö-dextrin did not begin to precipitate in the filtrate from the erythro-dextrin until the concentration of the alcohol reached 72%. These sharp limits of precipitation rather indicate that each of these dextrans is a pure substance. The transition temperature of this iodide is 33°. A 0.5% solution of erythro-dextrin is completely digested to the achromic point by 1:7 saliva in two minutes at the ordinary temperature. During the spontaneous fermentation of starch solutions containing no preservative but iodine, the starch passes through a stage in which the only color given with iodine water is the iodide of erythro-dextrin. (For other properties, see rose-amylose.)

Amylo-dextrin was clearly recognized and estimated in the filtrate of the slow digestion experiment just described. It gives a pure blue color with iodine-water which forms before the iodide of erythro-dextrin does in solutions containing both these substances. The transition temperature of the iodide is about 50°. Estimated in the filtrate by colorimetric comparison¹ with wheat starch boiled one hour, only 0.007% was present at the end of 15 minutes, only a trace at the end of 45 minutes, and none at the end of ninety minutes. Amylo-dextrin is, therefore, more readily digestible than erythro-dextrin, which it probably hydrolyzes into. The three dextrans already mentioned not only diffuse through the cell walls of the starch granules of bread, but also through goldbeaters' skin.

Red-amylose and a new substance which we will call *blue-amylose* require brief mention. Ordinary (unfiltered) digestion mixtures of bread or of boiled starch in which the amylose and the rose-amylose have been completely digested, as determined by the methods already given (that is to say, after five hours), and in which no erythro-dextrin is present, color a deep red on the addition of iodine-water in comparatively large amounts. The transition temperature of this iodide is 73°; but if the solution is heated somewhat above 80°, the red color no longer reappears on cooling the solution through 73°, but a blue coloration begins to appear as the solution is cooled through 83°. The substance giving the red color under these conditions agrees with Day's² description of red-amylose. It is probably a product of the hydrolysis of amylocellulose, and probably hydrolyzes into blue-amylose. Blue-amylose is best obtained by boiling

¹ Dermstedt, *Ber.*, 28, ref. 1025, among others, employed this principle.

² Day, *Loc. cit.*, 37, 41; Reichert, *Loc. cit.*, p. 195.

the residue of a digestion mixture after it no longer colors pink with small amounts of iodine-water (that is, after four hours).

A new dextrin giving with iodine-water a blue iodide (whence we may call it *cyanodextrin*) which forms before the iodide of rose-amylase in mixtures containing both these substances and the transition temperature of whose iodide is sharply 29.5° (uncor.), has also been recognized; but as it does not appear in the sequel of this paper, it will not be further discussed in this place.

It must be added, in order to avoid the erroneous deduction often met with in the literature¹ to the effect that potassium iodide changes the blue iodide of starch to red, that potassium iodide in solutions one-fourth saturated really destroys the blue iodide of starch, but does not affect the iodide of either rose-amylase or erythro-dextrin, even when added to saturation. This principle was confirmed by the fact that the amount of erythro-dextrin present in a mixture of dextrans and starch could be estimated colorimetrically in the presence of potassium iodide and alcohol (toward which reagent the red iodides are the more stable), even when the amount of starch present was varied within wide limits. Furthermore, solutions of blue iodides containing no erythro-dextrin, rose-amylase, or red-amylase do not turn purple or red on the addition of potassium iodide, but pass through green in disappearing.

Conditions of the Digestion.—All the materials used in these experiments were preserved with toluene (except takadiastase, which quickly molds in solution), and the digestions took place in the presence of toluene. The enzymes used were saliva, commercial ptyalin, Horlick's "diastoid," and takadiastase. The three latter were used in final concentration of 1%; the saliva in final concentration of 1 in 8, except where otherwise stated. The standard breads were prepared from the standard flours listed below, and were baked by standard commercial methods by J. C. Summers, of the School of Milling and Baking Technology, conducted by the *Operative Miller* of Chicago:

- No. 1. Kansas hard winter wheat flour.
- No. 2. Illinois soft winter wheat flour.
- No. 3. "Oriental," a spring wheat flour.
- No. 4. A standard commercial mixture.

The digestion mixtures usually contained 1% of the original material as their final concentrations, and all the results here recorded have been calculated to this basis. The polariscopic readings are all recorded as read on a Schmidt and Haensch half-shadow saccharimeter reading percentages of *d*-glucose in a 200 mm. tube. The interior of the loaves was used for digestion, either in the form of approximately 1-inch cubes or broken down completely by grinding in a porcelain mortar, except where

¹ Bayer and Field, *J. Chem. Soc. (Trans.)*, 101, 1403 (1912).

otherwise stated. This grinding does not disrupt the starch granules. In the experiments with cubes, which are not disintegrated by saliva, the results have been corrected for the amount of liquid removed for the separate readings. The digestions were carried out by mixing the materials at 25° and placing them in a water bath contained in an asbestos-lined air oven maintained at 37° . This procedure was adopted to simulate the conditions of normal digestion *in vivo*, the chilling effect of ingested food being observable for several hours. For the separate readings 25 cc. of the mixture were pipetted out into a beaker containing 2 cc. of a 1% solution of arsenic acid. This mixture was then filtered and the polarization read on the filtrate. When the starch granules begin to disintegrate (that is, after 4 or 5 hours), the fragments tend to run through the filter. Except where otherwise stated the polarizations have been corrected for the optical activity due to the sugars in the bread suspension by polarizing the filtrate from a suspension of inch cubes at the end of half an hour. Under these conditions most of the sugars but no dextrans enter the solution; and but little dextrin enters the solution even when the bread is completely broken down. The polarizations are also corrected for the optical activity of the diastoid and the takadiastase. The saliva and ptyalin were optically inactive. Takadiastase attacks both starch and gluten, and also slowly changes the maltose formed from the starch into *d*-glucose. The apparent acidity of the different materials used for digestion was obtained by titrating after half an hour the filtrate from broken down bread suspensions with 0.02 *N* potassium hydroxide and phenolphthalein, the recorded results having been corrected for the apparent acidity of the distilled water used in making the suspensions.

The following table gives the polarization of digestion mixtures made with the breads just described, the bread being in the condition known as "fresh" at the time of the digestion, except where otherwise stated. "Fresh" bread is that baked late in the day for sale the next day. Where the same bread was tested after different periods of fermentation, the digestion experiments were carried out simultaneously, in the same water bath. Three grams of the bread, in cubic form, were placed in the enzyme solution, the final volume being 300 cc. The bread floats throughout the experiment.

These results show, for hard and soft wheat flours, that the time of fermentation of the dough makes no appreciable difference in the digestibility when varied over a range of 400%; nor does such variation appreciably affect the acidity. They show, further, that the starch of the soft wheat digests nearly three times as fast as that of the hard wheat, the spring wheat and the commercial mixture acting approximately like the soft wheat. The digestion coefficients given in the table were obtained

TABLE I.
Polarizations Read as *d*-Glucose.

Wheat No.	Time of fermentation. Time of digestion (hr.).	1		2		3		4		Spotted yeast.		
		0.5 norm.	1 norm.	1 norm.	2 norm.	2 norm.	2 norm.	3 norm.	4 norm.	1 norm.	2 norm.	3 norm.
0.25		0.09	0.14	0.17	0.67	0.64	0.68	0.65	0.67	0.19	0.81	0.38
0.50		(0.18) ¹	(0.23) ¹	(0.26) ¹								
0.75		0.27	0.33	0.37								
1.50		0.55	0.64	0.62								
2.50		0.83	0.90	0.88	0.72	1.12	1.05	0.90	1.17	0.63	1.24	0.88
3.50		1.02	1.07	1.08	1.03	1.12	1.13	1.01	1.19	0.89	1.23	0.97
4.50		1.13	1.19	1.12	1.12	1.16	1.14					
5.50		1.13	1.17	1.14								
6.50		1.19	1.15	1.23								
22		1.21	1.21	1.34								
23					1.11	1.13	1.00					
45					1.09			0.96	0.94			
71					0.77	1.01	0.99					
316										0.89	1.00	0.70
Normal acidity.....	0.00019	0.00026	0.00010	0.00012	0.00012	0.00012	0.00012	0.00012	0.00012	0.00007	0.00007	0.00012
Original polarization....	0.08	0.00015	0.03	0.00	0.02	0.02	0.04	0.08	0.10	0.09	0.04	0.10
Digest. coeffic.....	15%	19%	22%	20%	56%	53%	57%	54%	56%	16%	67%	32%

¹ Interpolated.

by dividing the polariscopic reading at the end of one-half hour by 1.20 as an approximate average maximum.

The effects produced by the use of yeast which has begun to ferment owing to bacterial activity are marked in the cases of the bread from soft wheat and that from the "oriental" brand, the former being greatly accelerated, the latter retarded. Each of the breads made with spoiled yeast had a bitter taste. The ingestion of a small amount of one of these breads almost immediately caused a burning sensation in the stomach which lasted for ten hours, at the end of which time it was relieved by the ingestion of soda. Hence their digestion *in vivo* might differ still more than is here indicated for their digestion *in vitro*.

That the difference in the digestibility of the breads from hard and soft wheat flours is due wholly to differences in the amount of gluten these breads contain (8% and 6%, respectively), is shown by the following results, obtained by grinding in a mortar some of the pulp of the same loaves of bread used in obtaining the foregoing results. The duplicate determinations were made on the same suspension after standing three days in a glass-stoppered bottle, preserved by toluene.

TABLE II.
Duplicates.

Wheat No.	1 1/2	1	1 2	1 1/2	1	1 2	2 1/2	2	2 2
Time of fermentation.	norm.	norm.	norm.	norm.	norm.	norm.	norm.	norm.	norm.
Time of diges- tion(hrs.).									
0.25	0.91	1.12	0.97
0.50	1.08	1.01	1.17	1.09	1.02	1.13
0.75	1.01	1.16	1.18
1.50	1.05	1.08	1.04	1.09	1.13	1.14	1.05	1.08	1.04
2.50	1.08	1.05?	1.09	0.84	1.10	1.10
3.50	1.00	1.00	1.06	1.05	1.14	1.10	0.83	1.05	1.02
4.50	1.00	1.05	1.08
22	0.78	0.89	0.81	0.82	0.99	1.14?
23	0.89	0.97	0.94
71	0.79	0.89	0.79

The starch under these conditions in reality digests about as fast as boiled starch, as judged by the iodine colorations and the polariscopic readings (*infra*).

Other factors, such as slight variations in the acidity of the mixtures, in the temperature of mixing the digestion materials, and in the temperature at which the solutions were read on the polariscope exerted no appreciable effect.

The following results were obtained with three commercial breads, broken down under water just enough to cause the pulp to sink—a degree of disintegration approximately equal to that produced by normal mastication. The readings are uncorrected for the original polariza-

tions, since these were obtained on the pulp just described, instead of on the undisintegrated pulp, and hence the solutions contained appreciable amounts of dextrans.

TABLE III.

Bread No. Time of digestion. Hours.	5.	6.	7.
0.5.....	1.12	1.10	1.04
1.5.....	1.11	1.26	1.28
3.0.....	1.35	1.22	1.34
23	1.29	1.18	1.24
Normal acidity.....	0.00018	0.00015	0.00012
Original polarization.....	0.28	0.20	0.13

These results show that the disintegration of the gluten was sufficient to permit the digestion of the starch to the same extent as that in the breads ground up to flotation. That this agrees closely with the rate of digestion of freshly boiled starch is indicated by the results contained in the following table. The rice starch used in these experiments was boiled five minutes in approximately 2% solution. The concentration of dry (120°) starch in the digestion mixtures was 0.863%. This table also contains data on the digestibility of a home-baked bread (made with hard-wheat flour), and of another commercial bread. The interior of the loaf of these two breads was rasped on a horse-radish grater into fragments about 3 mm. in diameter. The results given in two of the columns were obtained on the same pulps air-dried. The results are not corrected for the original polarizations of the solutions. The starch at its final dilution polarized 0.64; but this seems to be mostly due to dextrans (as the amyloses filter out), which immediately digest, so that this correction should not be applied to the observed readings.

The initial maximum in the polariscopic readings obtained with the starch is due to the presence of a small amount of dextrans in the solution, even with 1 : 7 saliva, so rapid is the hydrolysis of the amyloses present. This may conveniently be shown with iodine after filtering off the rose-amylose, provided a preservative has been added to prevent the digestion of the erythrodextrin during filtration.

If the polarizations given for the starch be divided by 1.726 they become directly comparable with all the other results recorded in this paper, on the assumption that the breads contained 50% of starch, since all are calculated to 1% of the original material for the final concentration in the digestion mixture. This makes the values for the starch, even at the start, when the solution contained dextrans, only slightly higher than the corresponding values obtained with disintegrated bread pulp (Table II).

The colorations of the digesting starch with iodine-water show clearly the progress of the digestion of different ingredients in the starch. The original blue color was partly due to amylo-dextrin; the red color given at

TABLE IV.

Time of digestion. Hrs.	Color of starch with iodine-water in small amt.	Color with iodine due to	1% diastoid. Freshly boiled rice starch.	1% commercial ptyalin.			
				Home-baked bread No. 8.		Commercial bread No. 9.	
				Moist.	Air-dried.	Moist.	Air-dried.
0.00	Blue	Starch	0.64				
0.75				0.62		0.68	
1.00	Red → violet	Rose-amylose	2.62		0.25		0.28
1.75				0.96		0.86	
2.00	Pink → light purple	Rose-amylose	2.42		0.67		0.60
2.75				1.06		1.04	
		Rose-amylose					
3.00	Light purple	amylose	2.46		0.99		0.88
3.75				1.14		1.10	
4.00	Colorless		2.42		1.28		1.18
4.75				1.22		1.12	
	Large amount of Iodine-water		2.48 ¹		1.44		1.34
5.00	Purple	Red-amylose					
6.00	Purple		2.48				
		Red-amylose					
7.00	Purple	amylose	2.50				
		Red-amylose					
24	Trace of purple	amylose	2.70				
		Red-amylose					
25	Pink	amylose	2.60				
		Red-amylose					
26	Pink	amylose	2.64				

the end of one hour with iodine in small amount was due to rose-amylose, the dextrins and amylose having been nearly all changed into maltose; by the end of four hours the amylopectin and the rose-amylose were all digested; by the end of five hours the amylocellulose had digested sufficiently to disintegrate the walls of the starch granules (already disrupted by boiling), so that their fragments came through the filter paper, the mixture now containing red-amylose, requiring a large amount of iodine for the production of its iodide; by the end of twenty-four hours the amylocellulose was nearly all digested. The absence of any maltase (*infra*) is to be noted.

The low digestibility of the air-dried bread is probably attributable to the setting of the gluten during the drying, thus rendering the starch more difficult for the enzymes to get at, rather than to any change in the starch, as surmised by Neumann.²³ The home-baked bread was

¹ Filtrate turbid; refilter.

² *Zeit. ges. Getreidew.*, 6, 119 (1914); *Chem. Abs.*, 9, 2554.

³ Confirmed by direct experiment after complete disintegration of the gluten by grinding.

much more palatable than the commercial breads, but the polarizations show no reason therefor.

That the source and amount of the enzymes makes but little difference for moderate variation in amount in the rate of digestion of starch is indicated by the following results, obtained with the same bread pulp and the same starch solution, and the enzymes indicated in the table. Fernbach and Wolff¹ found that doubling the concentration of malt extract had no effect on the rate of digestion.

Time of digestion. Hrs.	1% rice starch.		1% home-baked bread.		
	1% diastoid.	1% takadiastase. (2.4) ²	1% com'l ptyalin.	1% diastoid.	1% takadiastase.
0.00					
0.50		1.94	(0.47) ³	0.43	0.40
0.75			0.62		
1.00	2.62	1.70		0.72	0.48
1.75			0.96		
2.00	2.42	1.65		0.92	0.47
2.75			1.06		
3.00	2.46			1.17	0.48
3.75			1.14		
4.00	2.42	1.51			0.46
4.75			1.22		
5.00	2.48	1.43			0.45
6.00	2.48				
7.00	2.50	1.35			0.44
24	2.70	1.18			
25	2.60				
26	2.64	1.16			0.44
29					0.45
122		0.92			0.22

The continuous fall in the readings obtained by the use of takadiastase is noteworthy. The initial value for the starch digestion was obtained by extrapolation, although the maximum must lie somewhere between time 0 and time 0.5 hour. The maximum obtained by extrapolation must be near the true maximum the solution would have shown, however, and agrees approximately with the values obtained by the use of diastoid.

The reason for the steady fall in the polarization obtained with takadiastase and starch is that the takadiastase contains maltase (as is well known³), so that the maltose slowly hydrolyzes into *d*-glucose. The final value obtained (asymptotically) after 122 hours equals 38.3% of the initial (extrapolated) value, in close agreement, considering all the circumstances, with the theoretical value 39.8%, based on the assump-

¹ *Loc. cit.*

² Extrapolated.

³ Daish, *Loc. cit.*, 2054.

tion that the initial optical activity was due to maltose and the final value was due to *d*-glucose, obtained by use of the formula

$$\text{Rotation of } d\text{-glucose} = \text{rotation of maltose} \times \frac{360}{342} \times \frac{52.5}{138.3},$$

where 52.5 is the specific rotatory power of *d*-glucose, 138.3 the specific rotatory power of maltose, and 360 the molecular weight of two molecules of *d*-glucose.

The one-half hour reading obtained by the action of takadiastase on bread also agrees fairly well with those obtained with other enzymes, although the actual amylase present in any of the preparations used was but a small indefinite per cent. of the total weight of the enzyme material. These results, therefore, together with the great activity shown by very dilute saliva, seem to indicate that the rate of digestion does not vary appreciably for moderate variations in the amount of enzyme present. Two influences in this case (takadiastase on bread) tend to diminish the polariscopic readings: first, the slow hydrolysis of the maltose to *d*-glucose; second, the digestion of the gluten, with the elimination of levorotatory substances. The value after 122 hours is only 19% of the average maximum polarization (1.20) of 1% bread preparations.

Takadiastase does not completely digest the amylocellulose even on long standing (122 hours), if it digests it at all; that is to say, if the residue is boiled at any time after the digestion mixture no longer gives any color with iodine-water (end of the digestion of amylopectin and rose-amylose), it will, on cooling, give a deep blue with iodine-water.

Conclusions.

1. The specificity and complexity of starches is confirmed.
2. A number of polysaccharides are clearly recognized and differentiated, and the existence of two new ones indicated.
3. The three principal ingredients of cereal starches are amylocellulose (the cell walls), amylopectin, and amylose.
4. The amylose, contrary to the contention of Maquenne and Roux, passes through the stages of amyloextrin and erythroextrin during salivary digestion, but these dextrins digest so rapidly that their presence in the digestion mixture can conveniently be demonstrated only when the enzyme concentration is very low (*e. g.*, 1 : 99). Furthermore, an appreciable amount of achroöextrin enters the solution with ordinary concentrations of saliva.
5. All of the dextrins under ordinary conditions disappear from the solution within 15 minutes, so that thereafter the further progress of the digestion can be followed by the polariscope, the only optically active substance then present being maltose if maltase has not been added from some outside source. As the amylose is all digested by this time, the

further digestion represents action on amylocellulose and amylopectin and their products of hydrolysis.

6. By slow digestion almost the entire amount of amylose present was obtained in solution as erythrodextrin at the end of 15 minutes. Hence under ordinary conditions the digestion of amylose must be almost instantaneous.

7. Rose-amylose, derived from amylopectin, digests completely in four hours. This has usually been regarded as the end of starch digestion, the rose-amylose being confused with erythrodextrin.

8. The amylocellulose (cell walls) digests only after more than 24 hours.

9. The only differences observable in the rate of digestion of bread made from hard or soft wheat, and fermented more or less than usual, were due to the relative amounts of gluten present. When the gluten was broken down the rate of digestion was sensibly the same.

10. The cause of the greater palatability of home-baked bread was not discovered.

11. Various pronounced effects due to fermentation by spoiled yeast were noted.

12. The activity of amylases is not sensitive to small changes of temperature or of acidity produced by the organic acids found in bread; nor does their activity seem to be proportional to their concentrations.

13. It would seem that under physiological conditions most of the amylose must be changed to dextrins in the mouth, and that these dextrins as well as most of the amylopectin and its products of hydrolysis must be digested in the stomach; whereas the digestion of the amylocellulose must take place for the most part in the intestine.

14. Stale (air-dried) bread digests very slowly unless its gluten be completely broken down.

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NEW BOOK.

Annuaire pour l'An 1916. Public par le Bureau des Longitudes. Price: 1.50 francs (30 cents). Paris: Gauthier-Villars & Cie.

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J. W. RICHARDS.



